

IMPROVED PROLOGIC BASIS SYSTEMS  
FOR CONTROL ANALYSIS

By

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to the Parents and Grandmother with Love

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Abstract of Dissertation Presented to the Graduate School  
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IMPROVED POLYOLIC BLENDED SYSTEMS FOR COATED METALLIC

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Twenty hydrazomethyl derivatives of heterocycles were obtained and their  $^{13}\text{C}$  NMR spectra were studied. Based on this  $^{13}\text{C}$  NMR study, the reaction between pyridine and pseudocyclotriphosphazene under alkaline condition was studied by  $^{13}\text{C}$  NMR spectroscopy using an inverse-gated decoupling technique. A mechanism which involved the final product 1,3-bis(hydrazomethyl)pyridine and intermediates 1-hydrazomethylpyridine, 1,1-bis(hydrazomethyl)pyridine, and 1,1,3-tris(hydrazomethyl)pyridine was proposed.

Also based on the first  $^{13}\text{C}$  NMR study of the hydrazomethylheterocycles, the copolymerization reactions of pyridine, hydrazopyridine, furan, and hydrazomethylfuran with phenol and hydrazophenols were studied with  $^{13}\text{C}$  NMR spectroscopy. The  $^{13}\text{C}$  NMR spectra of the reactions showed that copolymerizations did not occur. Therefore we used to copolymerize with phenol and formaldehyde to give resin with better physical properties.



Phenoxycyanide compounds containing phenol moieties were prepared and used to react with formaldehyde. Due to their low solubilities, no reaction occurred. Finally, copper phenoxycyanidebisacryloyl chloride was prepared and used to cross-link the phenolic prepolymer. It was found that the resulting modified phenolic resin was superior to the unmodified phenolic resin in a grinding test.

Epoxy and urethane-modified phenolic resins were also prepared, but they were found to be inferior to the unmodified phenolic resin in physical tests.

## CHAPTER I INTRODUCTION TO PHENOLIC RESINS

Phenolic resins are the cross-linked condensation products resulting from the reactions of phenols with aldehydes. Although unsubstituted phenol and formaldehyde are the most common monomers, other phenols such as cresols, bisphenol A, novolac, pyrogallol, guaiacol, tetrakisphenol and p-phenylphenol, and aldehydes such as formaldehyde and butyral are also used to modify the physical properties of phenolic resins. The molecular structure, which determines the physical properties of a phenolic resin, is affected by the structures of monomers, the phenol to aldehyde ratio, the nature and amount of catalyst, the reaction time and the reaction temperature, the method of degassing, the curing schedule, etc. Therefore, many synthetic options are possible, which in turn allows for a large number of possibilities for different physical properties and hence many applications for these products.

### 1.1 History

A. von Baeyer (1831-1906), 1873 Nobel, made the first studies of the phenol-aldehyde reaction in 1872 as an extension of phenol-based dye chemistry. Baeyer's original

was obtained but its properties suggested further attention at that time. Ter Meer [187428210], A. Claus and E. Trause [188028208] continued the experiments. In 1881 Claus and Trause obtained a soluble but non-crystallizable resinous material from a mixture of 2 moles of phenol, 1 mole of formaldehyde, and hydrochloric acid. In 1881 Kinsberg [188112211] obtained a cross-linked, insoluble resin by using an excess of formaldehyde and hydrochloric acid in a vigorous reaction. At that time there was still little interest in the products obtained.

In 1888, working independently, both Leobner [188428213] and Baerlein [188428146] prepared *p*-hydroxyphenyl alcohol which was found to have analgesic properties from an alkaline phenol-formaldehyde reaction at a low temperature. Five years later the first patent covering phenolic resins as a substitute for hard rubber was granted to A. Smith [188928212445]. However, the first commercial product was introduced as a shellac substitute in 1891 by Louis Hixson [18912817217].

The most important technical innovation was made in 1897 by Leo H. Baekeland who made possible the worldwide application of the polymer. His "heat and pressure" patent [18972812488, 18982812489] made economic production of molded parts possible by using pressure and high temperature, which permits a rapid curing cycle. Between 1897 and 1909, Baekeland conducted small-scale trials with a few industrial customers and patented numerous applications for phenolic resins. He made the first public disclosure in

a paper presented (1890189) before the American Chemical Society in 1889. In this and a slightly following paper (1890248), he described the alkaline catalyzed novolac resin and the acid-catalyzed thermoplastic product.

In 1889 Debus suggested calling the liquid novolac resin "resol" and Baekeland proposed the designation "novolac" for the novolac thermoplastic resin. New resins and novolacs, respectively, commonly refer to these two different types of resins. Another major contribution was made in 1914 by J.B. Aylsworth (189124894) who found that novolacs could be very economically cured by the addition of hexamethylenetetramine. In the same year, Baekeland founded the Bakelite Resin Company, and in Germany, the General Bakelite Company in Wm, and other companies later in England, France, Japan, and Canada. In 1916, the Bakelite Corporation was established, incorporating the competing National Chemical Products Company and the Condensate Company which was co-founded by Aylsworth. The Bakelite Corporation was taken over by the Union Carbide & Carbon Corporation in 1928.

The top five phenolic resin producers in 1986 were Borden Chemical, Georgia Pacific, Monsanto, DuPont-Corning Fibers, and Reichold Chemicals. The total annual production in USA alone in 1985 (189128894) was 440 million pounds. The production rose up to 500 million pounds in 1987 (189128894), well over a fivefold increase in 30 years.

The chemistry of phenolic resins has been extensively reviewed by R.W. Martin [19611962], R. Kemp and R. Schuch [19621963], R.A. Santapau [19621964], S.L. Meele [19621964], and by others in a symposium sponsored by the Superchemical Company [19621964].

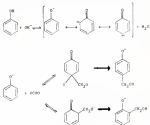
## 1.2 Resins and Novolacs

The phenol-formaldehyde reactions can be catalyzed by either acid or base. The rate of the reaction at pH 1 to 4 is proportional to the hydrogen ion concentration. Above pH 5, the rate increases with the hydroxide ion concentration, indicating a change in reaction mechanism. Depending on formaldehyde to phenol ratio, two types of phenolic resins, novolacs and novolacs, can be obtained.

### 1.2.1 Novolacs

When a catalyzed mixture of phenol and formaldehyde with a formaldehyde to phenol ratio greater than 1 is heated, a mixture of mono- and polymeric hydroxyethylphenols which contain hydroxymethyl side on end groups is obtained. When such a mixture is catalyzed with acid, the reaction becomes uncontrollable. However, when a base is used, the reaction is manageable and the prepolymer is called a novolac. Novolacs are thermosetting and can be cured by either heat or acid to give a three-dimensionally cross-linked, insoluble, and infusible polymer.

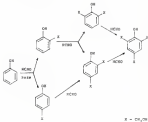
Under aqueous alkaline conditions, benzaldehyde exists mainly as hydrate and phenol is deprotonated rapidly by hydroxide ion to give the phenoxide ion which is stabilized by resonance. *o*-alkylation of the phenoxide ion occurs in both the *ortho* and *para* positions (Scheme 1.1).



SCHEME 1.1

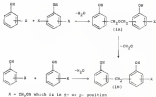
The exact nature of the hydroxyphenylating agent in the alkaline-catalyzed reaction is not yet fully understood. It is not clear how acetaldehyde could react with the phenoxide ion (STRASSER). The concentration of non-hydrated

formaldehyde is too low to explain the reaction rates. At an early stage of the reaction, monohydroxyethylphenols, dihydroxyethylphenols, and trihydroxyethylphenols are formed (Scheme 1.12).



**SCHEME 1.12**

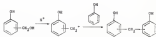
The monosubstituted hydroxyethylphenols continue to react in two ways: 1) formation of a debenzyl ether linkage (1a) which subsequently decomposes into a methylene bridge (1b) and 2) independent formation of a methylene bridge (Scheme 1.21).



SCHEME 1.1

The reactions of diaminodihydroxydiphenols, etc., continue similarly with further heating, and the molecular weight of the resin increases with reaction time. However, the reactions may be quenched by cooling when the desired molecular weight has been attained. In the next stage, the resin is cured by either heat or acid to give the final infusible, insoluble, cross-linked polymer. In the presence of acid, hydroxymethyl groups in the prepolymer decompose to benzylic carbocation ions (20) which quickly undergo *O*-alkylation of phenols (Scheme 1.2).

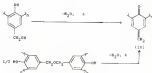




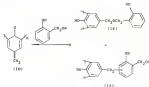
(10c)

SCHEME 1.4

If the dimer is cured by heat, quinone methides (10) are considered to be the intermediates [410855, 484240, 49178] which come from the elimination of water from related hydroxybenzylphenols or dihydroxy ethers (Scheme 1.5).

SCHEME 1.5

The quinone methides (18) cross-link with either hydroxymethyl groups to give dibenzyl ethers (19) or the *o*-H groups of phenols to give arylether linkages (20) (Scheme 1.2).



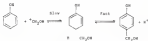
SCHEME 1.2

### 1.2.2 Resinols

When a mixture containing a formaldehyde to phenol molar ratio less than 1 is heated, a thermoplastic resin, called a *resinol*, is obtained. Usually an acid catalyst is used. However, an alkaline condition can also be used to produce a highly *glycol*-substituted resinol. Since phenol is used in excess, the condensation mixture contains oligomers with phenol end groups. The phenolic moieties are joined together linearly by methylene bridges. A resinol resin has

an ability to continue growing in molecular weight once formaldehyde has been consumed. Therefore, more formaldehyde or a cross-linking agent which provides additional formaldehyde is needed for curing the resin. The most widely used curing agent is hexamethylenetetramine (HMTA). Paraformaldehyde and trioxane are also used but are of limited importance.

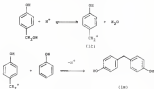
The first step of the reaction is the formation of hydroxymethylbenzene cation ion (100) from methylene phenol, which comes from the hydration of formaldehyde. This phenol is hydroxymethylated by this ion at either the para or ortho position (Scheme 1.7).



SCHEME 1.7

However, the hydroxymethyl group of the central products is unstable under acidic conditions and decomposes into the benzylic cationic ion (101) which reacts rapidly with another phenol molecule to give dihydroxydiphenylmethane

(180) (Scheme 1.8). Under acidic conditions, both hydroxyethylation and methylene bridge formation occur preferentially at the para position.

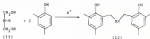


SCHEME 1.8

The first substitution on the phenolic nucleus substantially deactivates the ring against further substitution by formaldehyde. It is this difference between the acid and alkaline reactions that leads to polyphenol formation at high pH and linear chain growth at low pH. The dihydroxydiphenylmethane molecule can undergo further substitution but is not as reactive as phenol. Thus, in the early stage of the reaction, the amount of diphenol present increases rapidly while polyphenols are just beginning to be formed. The amount of polyphenols increases from the contribution of diphenols, etc., until all the formaldehyde

has been suggested. The potentially reactive third positions on the unsaturating prepolymer molecules are not completely deactivated and this leads to a small amount of branching. It is now generally accepted that acid catalysis tends to favor the formation of p,p'-linkages, although o,p'- as well as o,o'-linkages may also be formed.

Resin prepolymers must be cured by a cross-linking agent such as DETA. Reaction of DETA with the resin in the presence of water present in the prepolymer leads to the formation of unsaturated cyclic compounds such as bis(hydroxyethyl)oxirane (12). Carbocation ions are generated from these unsaturated cyclic compounds and react with phenolic moieties to form secondary tetrahydrones (12) and tertiary benzylium ions (Scheme 1-8).



SCHEME 1-8

### 1.3 APPLICATIONS

The single largest phenolic resin market is for unsaturated wood products, which include plywood, particle board, fiberboard, wafer board, and extruded wood

composites such as bones, stones, etc. Fiberglass alone came up 54% of the resin production in the USA (84000043181).

The thermal insulation industries grew rapidly during the 1970s as the prices of oil and gas increased sharply. The growth from 1970 to 1979 was over 218%. About 15% of the phenolic resin production is used as an insulation adhering to bind, for example, glass fiber and rock-wool filings.

The building compound market, which has been one of the largest traditional markets, has been in a steady decline and is expected to decline even further as other composite materials, such as engineered plastics, get a larger share of this market. However, good physical properties of strength and heat resistance give moderate cost keep phenolic resin in longstanding uses in the transportation, appliances, and electrical component markets. Today welded films are up 14% of the phenolic resin production.

A wide variety of applications exist for phenolic-bonded laminates that are based on paper, cotton, or glass substrates. Paper and paper-related industries utilize significant amounts of phenolic resin for making battery separators, filter media, high-pressure plastic laminates, and other similar commodities. Other uses include electronic circuit boards, gears, rods, bearings, tubes, furniture, wall paneling, and home and office furnishings.

Phenolic resins are also important in the foundry industry, where these resins are used to bind sands from

which various solids are made. The demand depends on the automotive and industrial machine industries.

About 21 of phenolic resin production ends up in abrasives. Phenolic-based abrasives are of two types: I) bonded abrasives including grinding wheels, mopping wheels, etc., and II) coated abrasives including sandpapers, disks, belts, etc.

Phenolic resins also have many other uses such as making primitive coatings, friction materials, and adhesives.

#### 1-4 Objectives

This research was sponsored by the Industrial Abrasive Division of 3M Company at St. Paul, Minnesota. The aim of this project is to improve the grinding performance of coated abrasive systems by changing the physical properties of the existing phenolic resins. This might be done either by changing the structure of the polymer by the use of modifiers or by the copolymerization with other monomers or prepolymers.

Coated abrasives, in the form of belts, disks, wheels and drums, are made by bonding a layer of abrasive grains onto a flexible backing by means of an adhesive. The abrasive grains may be aluminum oxide, silicon carbide, glass, emery, flint or garnet. The backings may be paper, fabric, fibers, or plastic. The adhesive is usually a phenolic resin because of its good impact strength, thermal

resistance and moisture resistance. First, the backing material is coated with the liquid resin. This coating is called the resin coat. Then the abrasive grains are deposited evenly on the resin coat by an electrostatic process. The loaded coating is dried and powdered before a second binder coat, the size coat, is applied. Finally both the resin and size coat are dried and cured. The curing process is the progressive polymerization of the prepolymer and involves the cross-linking of mainly linear oligomers.

To test the coated abrasive system, an abrasive belt is made according to the process described above and mounted on a grinding machine with 2 wheels. The belt is rotated at high speed while some carbon steel bars are pressed against the belt with pressure. The carbon steel bars are cut by the abrasive belt and heated red hot. The temperature may go up to  $1000 \sim 2000^{\circ}\text{C}$  in the surface layer. The weight loss of the steel bars is measured at different time intervals until the belt wears out. The total weight loss of the steel bars is a measure of the grinding performance of the abrasive system.

To perform well in the grinding test, the phenolic resin binder in this type of coated abrasive systems must have high thermal resistance so that it can stand the high surface temperature. The phenolic resin should have good adhesive property to hold the abrasive grains in the backing. The phenolic resin must also possess good mechanical properties such as hardness and toughness to reduce the mechanical impact from the carbon steel bars.



Therefore, the grinding performance of this type of coated abrasive systems may be increased by improving the thermal resistance, hardness, toughness and adhesive property of the phenolic resin binder.

These physical properties of the phenolic resins may be improved by changing their structure with chemical modifications; the different approaches to achieve these objectives are briefly outlined in section 1.4 and described in detail in the following chapters.

### 1.4 Phenolic Modification Methods

Phenolic resins have been modified by a large number of methods which are discussed below:

#### 1.4.1 Modification with Phenols

Substituted phenol is the most commonly used phenol. However, other phenols are also used to modify some physical properties of the resins. *p*-Cresol is used to improve toughness and thermostability of the resins [18110003]. Long chain alkylphenols give resins with increased flexibility and good compatibility with natural oil [18110005]. Modified phenolic resins from 1-butylphenol show excellent tack properties and good compatibility [7922P11791192]. Guercini reacts quickly with formaldehyde to give fast curing resins which can be cured at low temperature [18110006]. Bisphenol A can give resins

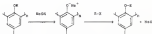
with improved color stability [40M24044]. Phenolic resins from *p*-substituted-phenol have high heat-resistance [89M013103; 894081].

#### 1.3.2 Condensations with Aldehydes

Boiled phenolic resins from formalal show enhanced flexibility and low viscosity [79R12809], and are useful for casting grinding and finishing materials. Acetaldehyde and butyraldehyde have low reaction rates with phenol, but they produce resins with less rigidity at high temperatures and are good rubber modifiers and antioxidants [79R12480]. Paraformaldehyde gives resins with good thermal stability and heat-curing rates [8002204; 800] Carbohydrates such as dextrins produce resins with good water resistance and tensile strength [80R12180018].

#### 1.3.3 Etherifications

The hydroxymethyl groups in phenolic prepolymers can easily be etherified with alcohols because of their tendency to form hydroxyphenoxyl anionium ions. The phenolic hydroxy groups can also be etherified with strong electrophiles such as alkyl halides, alkyl sulfates, epichlorohydrin, and epoxides in the presence of sodium hydroxide [Scheme 1.10].



R-X = alkyl halides, alkyl sulfates, epichlorohydrin, etc.

#### Scheme 1.12

These etherified phenolic resins have higher solubility in aromatic solvents, better dielectric, and higher alkali resistance and thermooxidative stability [KIRKPATRICK].

#### § 3.4 Sulfonations

The sulfonation of phenol rings in a novolac with aqueous sulfurous acids, such as phosphoric and sulfuric acid, or by reaction with phosphorus oxychloride can improve the thermal and flame resistance of the resin [TANIGUCHI]. Intermolecular cross-linking takes place predominantly with carbon novolacs, whereas with high  $\beta$ -hydroxyl novolacs sulfonation seems to be the preferred reaction [Figure 3.2].



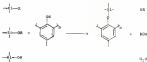
R = F, H

T = nHyl, nHyl, nH

FIGURE 1.1

### 1.4.2 Silicon-modified Resins

The hydroxy groups of a phenolic prepolymer can react with hexamethyldisiloxane, hydroxydimethylsiloxane, and octamethylcyclotrisiloxane to give resins with better thermal resistance [40,41,42,43] (Scheme 1.1).



SCHEME 1.1

### 1.3.4 Heavy Metal-modified Resins

Heat and flame resistant resins (HMRs) are obtained by the reactions of phenolic or phenolic resins with metal halides (e.g.  $\text{SnCl}_2$ ,  $\text{TiCl}_4$ ,  $\text{ZnCl}_2$ ,  $\text{SnCl}_4$ ), metal silicates (e.g.  $\text{SiOSnCl}_2$ ,  $\text{SiOTiCl}_2$ ), or organometallic compounds such as metal acetylacetonates.

### 1.3 Siloxanes

There are quite a lot of high temperature adhesives containing heterocyclic rings (HMRs), e.g. polybenzoxazines. It is expected that some heterocycles can impart higher thermal resistance into the copolymers. Therefore the heterocyclic derivatives of some benzoxazines, e.g. pyridic and furan, will be obtained and used to copolymerize with the phenolic prepolymers.

Some phthalocyanine compounds and polymers (HMRs) are well-known for their thermal stabilities. Some phthalocyanine compounds will be prepared and used to cross-link or copolymerize with phenolic resins.

It has been reported in the literature that epoxy-modified phenolic resins have improved toughness (toughening) and adhesive properties. Hence, some modifications of phenolic resins will also be attempted either by capping the phenolic hydroxy group with silyl group which then reacts with a 1-oxane polyepoxypropyleneamine, or by reacting the phenoxide groups in the prepolymer with

polyethylene glycols capped with glycidyl group as both ends.

Phenolic resins can also be modified with polyurethane prepolymers to improve the toughness. Hence some phenolic resins with urethane units will be prepared and their physical properties will be determined.

CHAPTER 1  
PREPARATION AND CARBON-13 NMR STUDY OF  
HYDROXYMETHYLATED CYCLES

1.1 Introduction

As mentioned in Chapter 1, one way to modify phenolic resins is to incorporate heterocycles or hydroxymethyl-heterocycles into the structure of the phenolic resins. To gain information on the structure of the modified resins, we planned to study them by  $^{13}\text{C}$  NMR spectroscopy. The  $^{13}\text{C}$  lines of the hydroxymethyl derivatives of heterocycles had, therefore, to be assigned to assist in the assignments of the  $^{13}\text{C}$  lines of the copolymer. For this reason, a number of hydroxymethyl derivatives of heterocycles were prepared or obtained commercially. The heterocycles involved were pyrazole, furan, 1,3-dimethylimidazole, thiophene, pyrimidine, and imidazole.

Pyrazole reacts with formaldehyde to give hydroxymethyl derivatives under basic conditions [18,19,20]. Pyrazole [18,19,20], imidazole [21,22,23], and 1,3-dimethylimidazole [20,24,25] also react with formaldehyde to yield hydroxymethyl derivatives with or without an alkaline catalyst.

However, hydroxymethyl derivatives of furan and thiophene have not been prepared by direct reactions with

formaldehyde. Under acidic conditions, furan gives isomeric, linear, open chain, and thiophene produces methylene-linked resins. Under basic conditions, neither of these compounds reacts with formaldehyde. Their hydroxymercapt derivatives must be prepared indirectly by other methods.

Several papers in the literature report the  $^{13}\text{C}$  chemical shifts of a variety of hydroxymercaptophenols [FRANKEIS, FIACCI, KATZMAN, MARCO] The ultimate goal of the studies was to use the  $^{13}\text{C}$  chemical shifts of the model compounds to assign those of actual phenolic resins and thus to determine their structures. To the best of our knowledge, no comprehensive  $^{13}\text{C}$  study of the hydroxymercapt derivatives of heterocyclic compounds has been reported previously in the literature, although the characterization of natural alcohol aldehydes by  $^{13}\text{C}$  is well-studied [KATZMAN].

### 1.3 Preparation of Hydroxymercaptophenols

Twenty hydroxymercapt derivatives of pyridine, furan, 2,5-dimethylpyridine, phenol, isidazole, thiophene, and pyrazole were obtained and studied. The structures of the compounds studied are shown in Figure 1.1





(29a)



(29b)



(29c)



(29d)



(29e)



(29f)



(29g)



(29h)



(29i)



(29j)



(29k)



(29l)



(29m)



(29n)

FIGURE 1

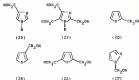
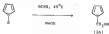


FIGURE 2.1 (Continued)

Compounds 121, 123, 125, 126, and 127 were obtained commercially from Aldrich. Compounds 124, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, and 139 were prepared according to literature methods. The other compounds, 120, 122, 124, and 126, were prepared according to the procedures described in the experimental section.

1-Hydroxyethylpyrrole (26) was prepared by heating a mixture of pyrrole and 1 mole equivalent of propionlaldehyde under acidic conditions at 45°C (Scheme 1-1). The hydroxyethyl group of 124 showed IR absorptions at 1376 and 1084-1010  $\text{cm}^{-1}$ , proton absorptions at  $\delta$  5.24(t) and 6.26(t) ppm, and  $^{13}\text{C}$  absorptions at  $\delta$  21.46 ppm. The symmetrical pyrrole ring gave two  $^{13}\text{C}$  lines at 284.75 and

129.79 ppm. The boiling point was found to be 45-46°C/1 mm (lit. bp 45.6-51°C/1 mm) [MAGGERS].



SCHEME 2.1

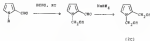
Compound (18a) was prepared according to the literature procedure [MAGGERS] by the reaction of 2-pyridonecarboxaldehyde with  $\text{KOH}$  in 45% yield (Scheme 2.1). The product showed IR absorptions at 1735 and 1685-1690  $\text{cm}^{-1}$ , but none in the nitrile region. There were five  $^{13}\text{C}$  lines which were assigned to the hydroxymethyl carbon (155.88 ppm) and the four different pyridine ring carbons (126.12, 140.38, 117.48, and 132.88 ppm). The boiling point was found to be 75-76°C/1 mm (lit. b.p. 81-85°C/1 mm) [MAGGERS].



SCHEME 2.2

1-(hydroxymethyl)-2-pyrrolacetic acididehyde was obtained by heating a mixture of 2-pyrrolacetic acididehyde and 1% formaldehyde for 3 hours (Scheme 2.2). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were consistent with the structure of the compound. The hydroxymethyl group gave rise to two  $^1\text{H}$  peaks at  $\delta$  5.43(m,4) and  $\delta$  2.91(m,4) ppm, and a  $^{13}\text{C}$  line at  $\delta$  21.83 ppm.

Compound (28), previously unknown, was prepared by reacting 1-(hydroxymethyl)-2-pyrrolacetic acididehyde with sodium borohydride in water at room temperature for 4 hours. The reaction of (28) with formaldehyde at  $1^\circ\text{C}$  for 2 days in the presence of NaOH gave (29) rather than (25). The purification of (29) was found to be difficult since it decomposed into (28) while passing through a silica gel column or upon distillation. The  $^{13}\text{C}$  spectrum of the crude (29) agreed with its assigned structure. Two lines at  $\delta$  54.87 and 49.48 ppm were assigned to the two hydroxymethyl carbons. The four different pyrrole ring carbons gave peaks at  $\delta$  186.83, 128.37, 121.53, and 112.29 ppm.



SCHEME 2.2

Compound (120) was prepared in quantitative yield by the reaction of pyridine with formaldehyde in the presence of a catalytic amount of NaOH at room temperature for 3 days. Pure (120) (98%) was obtained by washing the crude product with dichlorine methane (Scheme 3-4). This procedure gave a cleaner product than that obtained by the literature methods (17812082, 8928749448), which required higher temperatures. The  $^1\text{H}$ ,  $^{13}\text{C}$ , and IR spectra of this known compound were consistent with its structure. The melting point was found to be  $115\text{--}116^\circ\text{C}$  (lit. s.p.  $113\text{--}115^\circ\text{C}$ ) [4061684].



#### SCHEME 3-4

Compound (120), also previously unknown, was obtained by reacting (120) with a slight excess of 1%  $\text{NaOH}$  and water at room temperature for 3 days (Scheme 3-5). The crude product was purified by liquid chromatography with silica gel/hexane. The melting point was found to be  $85\text{--}100^\circ\text{C}$ . The  $^{13}\text{C}$  line at  $43.46$  ppm and  $^1\text{H}$  absorptions at  $\delta$  3.13 (d) and 3.48 (12,12) indicated that a  $\text{S-CH}_3$  group was present in its structure.



SCHEME 1.3

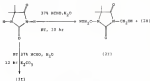
The 5,5-dimethylpyridazinone reacted with 37% formaldehyde without a catalyst at  $4^{\circ}\text{C}$  for 18 hours to give 1-hydroxyethyl-5,5-dimethylpyridazinone (22) (HMPT8412) (Scheme 1.4). The  $^1\text{H}$  and  $^{13}\text{C}$  spectra were consistent with the structure of (22).



SCHEME 1.4

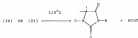
When the above reaction was carried out at room temperature, a mixture of (22) and 1,3-bis(hydroxyethyl)-5,5-dimethylpyridazinone (23) was obtained in about 1:1 ratio (HMPT81047). However, (22) was the only product isolated when potassium carbonate was used as the catalyst (Scheme

2.1) the  $^1\text{H}$  and  $^{13}\text{C}$  spectra were consistent with the structure of (15).



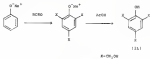
SCHEME 2.1

Neither (18) nor (17) was considered to be a potential modifier for phenolic resins since both compounds decomposed to 3,5-dimethylpyridazine and formaldehyde below temperatures required for curing the modified resins (Scheme 2.2).



SCHEME 2.2

2,4,6-Trisubstitutedphenol (12L) (349835T) was prepared by the reaction of sodium phenoxide with excess bromide at room temperature, followed by neutralization with acetic acid in acetic acid (Scheme 2.3). The  $^{13}\text{C}$  spectrum showed that a mixture of 12L and 2,4,6-trisubstitutedphenol was obtained. Compound 12L showed peaks at 88.34, 43.43, 125.45, 128.84, 131.83, and 155.58 ppm.



### SCHEME 2.3

Heating a mixture of imide and 5% aqueous NBSO in a sealed tube at  $120^\circ\text{C}$  for 24 hours gave a mixture of 1-hydroxy-2-substitutedimidazole (2R) (2R), 2-hydroxy-3-substitutedimidazole (2R) (2R), 2,4,6-trisubstitutedimidazole (2R) (2R) and other compounds (349835T) (Scheme 2.4). Compound 12R showed a characteristic  $\text{O}-\text{CH}_2\text{OH}$  peak at 61.51 ppm whereas 12R showed a  $\text{C}-\text{CH}_2\text{OH}$  peak at 58.85 ppm. Compound 12R had two different  $\text{O}-\text{CH}_2\text{OH}$  groups whose  $^{13}\text{C}$  lines were at 54.55 and 54.58 ppm.





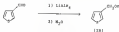
SCHEME 2.12

4-(5-Hydroxymethyl)furan-2,5-diol (122) was prepared by treating furan with a mixture of formaldehyde, ammonia, and basic cupric carbonate (Baker's) (Scheme 2.12). The hydrochloride salt of (122) exhibits  $^{13}\text{C}$  peaks at 51.29, 115.59, 126.29, and 133.75 ppm. The natural compound gave peaks at 133.82, 131.64, 115.42, and 51.26 ppm. The melting point was found to be 78–81°C (lit. m.p. 75–80°C) [Kobayashi].



SCHEME 3-11

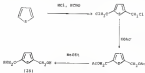
3-Hydroxyethylthiophene (18) was prepared by the reduction of 3-thiophenecarboxaldehyde with lithium aluminum hydride (Scheme 3-11). The IR spectrum showed no carbonyl peak, but the characteristic broad hydroxy peak was seen at 3300-3400  $\text{cm}^{-1}$ . The  $^{13}\text{C}$  spectrum showed the hydroxyethyl carbon at 85.05 ppm. The yield was 48-75%. The boiling point was found to be 22°C/4mm (lit. b.p. 26°C/15mm) (1873).



SCHEME 3-12

2,5-Bis(hydroxymethyl)thiophene (19) was obtained by bubbling hydrochloride gas into a solution of thiophene and formaldehyde, then stirring 2,5-bis(chloromethyl)thiophene with potassium acetate, and finally heating 2,5-

bis(methoxymethyl)lithiophane with sodium ethoxide in ethanol at room temperature [48JA1618] (Scheme 2.11). The  $^{13}\text{C}$  spectrum with peaks at 145.41, 118.86, and 88.88 ppm was consistent with the assigned structure. The boiling point was found to be 279-279°C/0.8mm (lit. b.p. 181-184°C/0.3mm) [48JA1618].



SCHEME 2.11

2-Hydroxymethylglyoxal (12) was prepared by oxidizing a lithium salt of glyceral and 37% aqueous HCHO at room temperature for 18 hours [48JA1618] (Scheme 2.11). The hydroxymethyl O-H band appeared at 3210-3180  $\text{cm}^{-1}$  in the IR spectrum and the carbon at 73.89 ppm in the  $^{13}\text{C}$  spectrum. The melting point was found to be 88°C (lit. m.p. 80-82°C) [48JA1618].



SCHEME 2.14

### 2.1 Jackson-ES NMR Study of Hydroxymethylfuranosides

The  $^{13}\text{C}$  NMR spectra were recorded with a Varian XL-300 NMR spectrometer. Deuterated DMSO was used as the solvent for all samples because it dissolves both the polar hydroxy compounds and the cyclic samples, the spectra of which will be discussed in later chapters. The use of a single solvent was desirable since we could compare the chemical shifts without considering the solvent effect.

The chemical shifts of the hydroxymethyl derivatives of the heterocycles are listed in Table 2.1:

The chemical shifts of compounds (30) [K102798], (32), (38), and (44) [79812038], [90114914] reported in the literature are in good agreement with ours although small differences arise from solvent effects. The assignments for compounds (44), (38) and (44) are straightforward since the structures are symmetrical: carbons C1 and C5 appear at 105.4-106.8 ppm which are close to that of the unsubstituted



pyridine (187.84 ppm); Carbons C3 and C5 of (24) give a signal at 120.76 ppm and compounds (26) and (28) show peaks at 122.2-123.3 ppm for the same carbons. The hydroxymethyl groups of (24), (26) and (28) give signals at 54.8-58.8 ppm when attached to C2 or C6 and at 45.5-52.8 ppm when attached to the nitrogen. Based on the chemical shifts of compounds (26), (28), (32), and unsubstituted pyridine, the chemical shifts assignments of compounds (26) and (32) are unambiguous.

In compounds (26) and (32), the  $^{13}\text{C}$  shifts are well separated and the assignments are obvious except those for the two hydroxymethyl groups of compound (32). Moreover, C3 should be at lower field than C5 because the former is subject to the electronic effect of two adjacent methyl groups whereas C5 is next to only one. Similar comparisons arguments lead to the same conclusion.

For compound (28), the assignments of C3 and C5 are easy. Carbon C4 should be lower field than C6 since the former is adjacent to a pyridine-like nitrogen whereas the latter is next to a pyridine-like nitrogen. Compounds (26) and (32) are symmetrical, therefore there is no problem to assign the lines. With the help of the APT technique, the C3 and C5 lines of (28) are distinguished.

The symmetrical structure of (28) makes the assignments of the lines unambiguous. The assignments of the lines of (28) and (32) are made by comparing them with those of 1-methylpyrrolidine (486118712) and 1-methylpyrrolidine (48611871), respectively.

### 2.3.3. Chemical shifts of hydroxymethyl carbons: Effect of heterocyclic rings.

The  $^{13}\text{C}$  chemical shift of  $\text{CH}_2\text{OH}$  is 49.3 ppm. Table 2.1 contains the shifts of 8  $\text{CH}_2\text{OH}$  carbons attached to heterocyclic nitrogens; they lie in the range of 43.3 - 71.4 ppm. Within this range, the shift depends on the type of the nitrogen: lowest for amine-N (compounds 1B and 1C); intermediate for pyridine in which additional  $\text{C}-\text{CH}_2\text{OH}$  may decrease the shift (compounds 1A, 1C, and 1D); and highest for imidazole and pyrazole (compounds 1E and 1F).

Table 2.1 also contains the shifts of 17 unique  $\text{C}-\text{CH}_2\text{OH}$  groups; they lie in the range of 33.5 - 61.6 ppm. Within this range,  $\text{CH}_2\text{OH}$  groups attached to pyrazine, furan and imidazole fall at the low end, those attached to thiophene are intermediate, and those to phenol (especially at the *o*-position) are at the high end. There is an simple relationship between these shifts and the  $\sigma$ -constants for the heterocyclic rings to which they are attached:

### 2.3.4 Effect of hydroxymethyl group substitution on ring carbon shifts.

Substituent effects of the hydroxymethyl groups on pyridine, furan, thiophene, imidazole, and pyrazole ring carbon chemical shifts are determined and listed in Table 2.2. For example, the substituent effects on pyridine of hydroxymethyl group at the 31 and 41 positions are calculated by comparing the chemical shifts of compounds

Table 3.2 The Effects of Hydroxymethyl Group Substitutions on Ring Carbon Shifts

Ring System	Substituent	CH <sub>2</sub> OH Position	C1	C2	C3	C4
Pyrazole	1a	1-	+1.08	+1.23	+0.17	+0.04
Pyrazole	1b	1-	+18.87	+1.42	+0.55	+0.14
Pyrazole	1c	1,2-	+18.87	+1.42	+0.83	+0.91
Pyrazole	1d	2,5-	+14.54	+1.10	+1.90	+14.14
Pyrazole	1e	1,2,5-	+15.70	+0.40	+0.60	+15.13
Furan	1f	2,5-	+11.00	+2.00	+2.00	+12.00
Furan	1g	1-	+11.00	+1.10	+1.10	+0.14
Imidazole	2h	1-	+5.74	/	+0.61	+0.70
Imidazole	2i	1-	+11.77	/	+0.60	+0.60
Imidazole	2j	4-	+0.80	/	+10.40	+1.00
Imidazole	2f	2,4,5-	+14.17	/	+10.07	+10.27
Thiophene	2k	1-	+20.91	+1.40	+0.53	+0.14
Thiophene	2l	1-	+5.24	+10.10	+0.40	+0.00
Thiophene	2m	2,5-	+15.00	+0.30	+0.70	+10.04
Pyrazole	2r	1-	/	+0.00	+3.00	+0.07

Notes: The chemical shifts of pyrazole in CD<sub>3</sub>-OH are at 111.63 and 107.54 ppm; furan at 142.54 and 100.50 ppm; imidazole at 121.90 and 115.40 ppm; thiophene at 126.04 and 119.07 ppm; pyrazole at 110.00 and 101.00 ppm.



(116) and (120), respectively, with the chemical shifts of unsubstituted pyrolic:

Ring carbon atoms attached directly to a  $\text{CH}_2\text{OH}$  group are subjected to a down-field shift of 18.3 to 20.5 ppm (17 examples). Within this range, thiophene is shifted most; pyrolic in intermediate, furan and imidazole are least affected.

The other ring carbon atoms are much less affected; shifts of -1.1 to 61.8 ppm are found. The carbons adjacent to the point of attachment show the greatest shifts, and the shifts decrease as the distances between the carbons (8-, 6-, and 4'-positions) and the  $\text{CH}_2\text{OH}$  group increase. This trend indicates that the effect is mostly inductive.

#### 2.4 Conclusions

The  $^{13}\text{C}$  assignments of the hydroxyacetyl derivatives of the heterocycles provide useful information for the  $^{13}\text{C}$  NMR study of the reaction of pyrolic and pseudouracilic acids, which will be discussed in the next chapter. It is also helpful in the study of the copolymerizations of phenol, furanolic acids and the hydroxyacetyl derivatives, which will be discussed in chapter 4.

The hydroxyacetyl group has similar substitution effects on the heterocyclic ring to those of the methyl group. This can be seen from the similarities in ring chemical shifts between 2-methylimidazole (118.3, 118.8 and

128.3 ppm) (400218181), 1-methylpyrrole (128.7, 125.1 and 128.3 ppm) (400218173) and 3-methylthiophene (125.1, 126.2, 125.1 and 128.1 ppm) (400218712) and 1-hydroxymethylindazole (127.5, 128.8, 128.1 ppm), 1-hydroxymethylpyrrole (128.3, 126.9, 129.4 ppm) and 2-hydroxymethylthiophene (123.1, 124.1, 127.2 and 128.3 ppm) correspondingly.

## 2.5 Experimental

### 2.5.1 $^{13}\text{C}$ NMR Measurement

Carbon-13 NMR spectra were obtained on a Varian XL-100 NMR spectrometer operating at 50 MHz with  $\text{d}_6\text{-DMSO}$  as the solvent at ambient temperature. Sample concentrations were about 15%. Pulse widths were 1.5  $\mu\text{s}$  and there was no pulse delay.  $\text{d}_6\text{-DMSO}$  was used for lock and the methine peak at 76.8 ppm was used as the reference.

Reagent-grade model compounds (2P), (2P), (2I), (2O) and (2P) were purchased and used without further purification. The following were prepared by the literature methods: Indazole, b.p. 45-52°C/1.5mm (lit. b.p. 45-52°C/1.5mm) (34261191), 2-hydroxymethylpyrrole, b.p. 75-77°C/1.5mm (lit. b.p. 71-80°C/2mm) (34261191), 1-hydroxymethyl-3,5-dimethylhydantoin, m.p. 91-101°C (lit. m.p. 110-117°C) (378125609), 1,3-bis(hydroxymethyl)-3,5-dimethylhydantoin, m.p. 88-90°C .

2,3,5-tris(hydroxymethyl)phenol, m.p. 19-21°C (lit m.p. 19-20°C) (12,26,187); 1-hydroxymethylisobutanoic (pinic) acid, m.p. 102°C (lit m.p. 200-210°C) (31,32,188); 2-hydroxymethylisobutanoic (2CI), m.p. 112°C (lit m.p. 110-112°C) (18,189); 4-hydroxymethylisobutanoic acid, m.p. 89-91°C (lit m.p. 89-90°C) (13,190,141); 2,3,5-tris(hydroxymethyl)isobutanoic acid, m.p. 218°C (lit m.p. 210-212°C) (18,191,192); 2,3,5-tris(hydroxymethyl)thiophene, b.p. 170-178°C/0.4 mm (lit b.p. 163-166/0.2 mm) (19,20,142); 3-hydroxymethylphenol, m.p. 88°C (lit m.p. 88-90°C) (18,193,194).

### 3.5.3 Preparation of 1,2-bis(hydroxymethyl)glycolic (18)

A mixture of 2-pyrrolidonecarbaldehyde (1.0 g, 9.531 mmol) and 1% aqueous KOH solution (1.7 g, 9.531 mmol) was heated in a steam bath in a 10 ml round-bottomed flask for 3 hours. Water was removed from the solution under reduced pressure. The crude 1-hydroxymethyl-2-pyrrolidonecarbaldehyde was not purified because it was unstable and decomposed into 2-pyrrolidonecarbaldehyde at room temperature. The compound decomposed upon distillation. The  $^{13}\text{C}$  NMR spectrum of the crude mixture showed that 40% of the 2-pyrrolidonecarbaldehyde was converted into 1-hydroxymethyl-2-pyrrolidonecarbaldehyde:  $^1\text{H}$  NMR (CDCl<sub>3</sub>)  $\delta$  5.4 (m, s), 2.80 (m, s), 4.23 (t, s), 6.43 (m, s);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>)  $\delta$  71.31, 118.89, 126.47, 131.50, 131.78, 166.29. 1-hydroxymethyl-2-pyrrolidonecarbaldehyde (0.40 g, 3.8 mmol) was dissolved in 5

ml of water to a 25 ml round-bottomed flask. A solution of  $\text{SnCl}_4$  (8.4 g) in 2 ml of water was added over a period of 15 minutes. After 1 hr, the emulsion was extracted with  $\text{Et}_2\text{O}$ , and extracted with ether (about 50 ml). The ethereal extracts were combined and the solvent was removed under reduced pressure. The crude product decomposed into 2-hydroxyethylpyrrole while passing through a  $\text{CaH}_2$  column or upon distillation. The  $^{13}\text{C}$  spectrum showed that the product mixture contained both compound (2c) and 2-hydroxyethylpyrrole.  $^{13}\text{C}$  ppm for (2c) ( $\text{CDCl}_3$ -MSD):  $\delta$  14.17, 44.88, 104.43, 108.77, 121.53, 130.35.

#### 2.4.3 Preparation of 2,3-bis(hydroxyethyl)pyrrole (2d)

A mixture of pyrrole (4.7 g, 8.4 mmole), paraferric chloride (5 g) and 10 ml water solution (5.1 ml) was stirred at room temperature for 3 hr in a 25 ml round-bottomed flask. The white solid was poured into 50 ml of  $\text{CHCl}_3$  and the suspension was stirred and then filtered. The white solid was washed with  $\text{CHCl}_3$  and then dried under a vacuum desiccator. The yield was 3.88 g (44.5%).  $^{13}\text{C}$  ppm ( $\text{CDCl}_3$ -MSD):  $\delta$  4.43(48.3), 4.88(20.4), 5.88(28.46, 18.62(28.36),  $^{13}\text{C}$  ppm ( $\text{CDCl}_3$ -MSD):  $\delta$  14.54, 105.44, 108.19, 10 (avg) 1000-2000, 1600, 1470, 1000  $\text{cm}^{-1}$ , n.p., 105-110°C (lit., n.p., 112-118°C (448)(2038)).

#### 2.5.4 Preparation of 2,5-bis(hydroxymethyl)pyrrole (18)

A mixture of 2,5-bis(hydroxymethyl)pyrrole (8.55 g, 0.05 mole) and 17% aqueous NaOH solution (5 mmole) was stirred at room temperature for 3 days. Water was removed under reduced pressure. The crude product was purified by column chromatography with  $\text{EtOAc}/\text{hexane}$ . The yield was 8.45 g (96.8%).  $^{13}\text{C}$  NMR ( $\text{d}_2\text{-DMSO}$ ):  $\delta$  55.55, 65.55, 108.88, 133.33;  $^1\text{H}$  NMR ( $\text{d}_2\text{-DMSO}$ ):  $\delta$  4.45(4H,d), 4.45(2H,t), 5.10(2H,d), 5.44(2H,t), 18 (impure) 1620-1580, 1671, 1595, 1514, 1545, 1479, 1325, 1318, 1445, 945, 945, 748, 748, 708  $\text{cm}^{-1}$ ; m.p. 98-100°C.

#### 2.5.5 Preparation of 3-hydroxyisothiazolidinone (19)

To a THF (18 ml) suspension of  $\text{LiAlH}_4$  (4.18 g, 0.81 mole) in a 100 ml 3-necked round-bottomed flask fitted with a magnetic stirrer, a gas inlet, and a septum, a THF solution of 3-thiaphenecarboxaldehyde (1.12 g, 0.01 mole) was added dropwise under an argon atmosphere at 0°C. Stirring was continued at room temperature for 3 hours. The mixture was poured over ice (50 g) immediately and then  $\text{CO}_2$  gas was bubbled through the solution until it was neutral. The solution was extracted with ether (3x100 ml). The ethereal extracts were combined and dried over  $\text{P}_2\text{O}_5$ . The solvent was removed under reduced pressure and the residue was distilled. The yield was 0.33 g (28.75% b.p. 70°C/0.5mm Hg, b.p. 90°C/15mm (8/10/75)).  $^{13}\text{C}$  NMR ( $\text{d}_2\text{-DMSO}$ ):  $\delta$  144.34,

$127, 131, 139, 147, 151, 211, 223, 443, 467, 509, 523, 547, 587, 607, 647, 683, 707, 739, 767, 787, 809, 823, 857, 883, 907, 937, 967, 997, 1013, 1039, 1067, 1093, 1117, 1151, 1187, 1213, 1237, 1271, 1297, 1327, 1361, 1397, 1433, 1469, 1511, 1547, 1583, 1619, 1661, 1697, 1733, 1771, 1811, 1847, 1889, 1931, 1973, 2017, 2063, 2107, 2153, 2201, 2249, 2297, 2347, 2399, 2453, 2507, 2561, 2617, 2671, 2729, 2789, 2849, 2909, 2969, 3029, 3091, 3151, 3211, 3271, 3331, 3391, 3451, 3511, 3571, 3631, 3691, 3751, 3811, 3871, 3931, 3991, 4051, 4111, 4171, 4231, 4291, 4351, 4411, 4471, 4531, 4591, 4651, 4711, 4771, 4831, 4891, 4951, 5011, 5071, 5131, 5191, 5251, 5311, 5371, 5431, 5491, 5551, 5611, 5671, 5731, 5791, 5851, 5911, 5971, 6031, 6091, 6151, 6211, 6271, 6331, 6391, 6451, 6511, 6571, 6631, 6691, 6751, 6811, 6871, 6931, 6991, 7051, 7111, 7171, 7231, 7291, 7351, 7411, 7471, 7531, 7591, 7651, 7711, 7771, 7831, 7891, 7951, 8011, 8071, 8131, 8191, 8251, 8311, 8371, 8431, 8491, 8551, 8611, 8671, 8731, 8791, 8851, 8911, 8971, 9031, 9091, 9151, 9211, 9271, 9331, 9391, 9451, 9511, 9571, 9631, 9691, 9751, 9811, 9871, 9931, 10000) = 0$

CHAPTER 1  
QUANTITATIVE STUDIES AND STUDY OF THE REACTION  
OF PYRROLE WITH FORMALDEHYDE

### 1.1 Introduction

There are few references to the reaction between pyrrole and formaldehyde in the literature. In 1938, Challinor and Roberts [1A18P188] prepared 1,5-bis(hydroxymethyl) derivatives of pyrrole and 3-methylpyrrole. Later Toppert and Richter showed that 1-hydroxymethylpyrrole can also be obtained by the condensation of formaldehyde with pyrrolopyrrolone lactone or with pyrrole and sodium hydride as catalyst [3A1A1285]. In the presence of potassium carbonate, pyrrole reacts with formaldehyde at 60-80°C to give 1-hydroxymethylpyrrole which disproportionates to pyrrole and 1,5-bis(hydroxymethyl)pyrrole upon heating [5Fen18452, 4F5682481414]. In the presence of sodium, pyrrole and formaldehyde yield pyrrole-5-methylamine [1A18P213]. This reaction has been used to prepare polyamine polymers [1A1PACT12].

Until now, there has been no thorough study of the reaction. Therefore, we have carried a detailed study of the reaction between pyrrole and paraformaldehyde in the presence of sodium hydride using  $^{13}\text{C}$  NMR spectroscopy.

to monitor the reaction. The reaction could produce up to four different hydroxymethylglycerols (Figure 3.1), which were 1-hydroxymethylglycerol (18), 1,2-bis(hydroxymethyl)glycerol (19), 1,2,5-tris(hydroxymethyl)glycerol (20), and 2,5-bis(hydroxymethyl)glycerol (21), with while bisformate 3-hydroxymethylglycerol (22) was not found on the reaction.

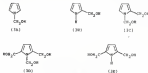


FIGURE 3.1

### 3.2 results

The reaction was studied with the interrupted decoupling technique. Samples were taken out at different time intervals, quenched at low temperature to halt the reactions and their  $^{13}\text{C}$  spectra were recorded.

A little D $_2\text{O}$  ammonia solution (90%) ml was added to each NMR sample to decompose bisformate of the hydroxymethylglycerols which otherwise was found at the beginning of the reactions in quite significant quantity and



which made the assignments and calculations difficult. The chemical shifts of the reaction products were affected slightly by the addition of ammonia solution. For example, the sample after 20 minutes at  $45^{\circ}\text{C}$  consisted a mixture of 1-hydroxyethylpyrrole (Ib), the hemiformal of (Ia) and unreacted pyrrole. 1-hydroxyethylpyrrole gave  $^{13}\text{C}$  lines at  $\delta$  71.45, 125.71 and 118.29 ppm, and pyrrole showed  $^{13}\text{C}$  lines at  $\delta$  117.42 and 127.81 ppm. After ammonia solution was added, the chemical shifts of (Ib) and pyrrole changed to  $\delta$  71.44, 125.65, 118.28 ppm and  $\delta$  118.15, 128.27 ppm respectively. The small shift may be attributed to a change in solvent polarity because of the small amount of water and ammonia in the ammonia solution.

The addition of ammonia solution suppressed the  $^{13}\text{C}$  lines of the hemiformal of (Ia) at  $\delta$  124.81 (2,3-ring carbons), 125.19 (3,4-ring carbons), 85.31 ( $\text{O}-\text{CH}_2-\text{OH}$ ), and 74.47 ( $\text{O}-\text{CH}_2-\text{OH}$ ) ppm completely. A comparison of the integrals of the lines at  $\delta$  122.81, 125.79 and 118.31 ppm before ammonia addition and the integrals of the lines at  $\delta$  118.45 and 118.31 ppm after ammonia addition showed that the hemiformal was decomposed completely into (Ib) and formaldehyde. The ratio of the total of (Ib) together with its hemiformal to pyrrole was found to be 53 : 43 which was exactly the same as the ratio of (Ib) to pyrrole after the addition. The phenol analogue, 1-hydroxyethylphenol, also formed a hemiformal with formaldehyde (FMAPF) with the  $\text{O}-\text{CH}_2-\text{OH}$  peak at 85.3 ppm.

To find a suitable pulse delay time (which should be at least 5 times that of the longest  $T_1$ ) for the inverse-gated decoupling NMR experiments,  $T_1$  relaxation time measurements were carried out for the five hydroxyanthrypyrones and pyrone. The  $T_1$  values for the carbons of the compounds were determined and are listed in Table 3.1.

Table 3.1 The  $T_1$  Values (in sec) for the Carbons of Pyrone and the Five Hydroxyanthrypyrones.

<u>Carbon</u> <u>Positions</u>	<u>C2</u>	<u>C3</u>	<u>C8</u>	<u>C9</u>	<u>C6</u>	<u>C7</u>
Pyrone	0.81	0.37	0.27	0.82	/	/
1a	1.24	1.00	1.00	1.14	1.20	/
1b	0.84	0.72	0.60	0.70	/	0.71
1c	0.80	0.60	1.31	0.82	0.36	0.81
1d	10.10	0.40	0.83	10.04	/	0.86
1e	0.10	0.10	0.20	0.10	0.22	0.31

From the  $T_1$  values in Table 3.1, we can see that some general trends of the effects of structure on the spin lattice relaxation time. First, the smaller the molecule, the longer the  $T_1$ . As the sizes of the molecules increase down the table, it is found that the  $T_1$  values decrease down the table. Second, the  $T_1$  of the carbons which are directly bonded by hydrogens are relatively short whereas quaternary carbons have longer  $T_1$  values. It is seen that the quaternary carbons in the table have  $T_1$  values between 5-10 seconds and the CH carbons have values less than 1.1 seconds. Third, symmetrical molecules have longer  $T_1$

carbamates since their methoxycarbonyl analogues. For example, the carbons of (3C) have longer  $T_1$  times than those of (3E) since the former is more open-chain than the latter, although they are similar in size.

At the very beginning of the reaction, the reaction mixture contained pyrrole, (3A), and (3E). The peaks at 117.42 (pyrrole), 126.76 (3A), and 121.53 (3E) ppm were used to calculate the mole fractions of the compounds because these peaks were better separated than those between 184-188 ppm. Since the pyrrole peak at 117.42 ppm had the longest  $T_1$  value (8.55 seconds), a pulse delay time of 18 seconds was used for the samples containing pyrrole. If the samples did not contain pyrrole, the well-separated chemical shifts of the hydroxymethyl groups between 54-73 ppm were used for calculations. The longest  $T_1$  among them was 5.55 seconds. Therefore a pulse delay of 8 seconds was used for samples without pyrrole. When the samples contained all compounds, both sets of peaks were used for calculations and the pulse delay time was 18 seconds.

At 0°C, the  $^{13}\text{C}$  spectrum of the reaction mixture after 20 days contained mainly 1-hydroxymethylpyrrole (3A) together with free formaldehyde, pyrrole and a small amount of the residues of (3A).

Heating for one month at 0°C gave a mixture of 1-hydroxymethylpyrrole (3A), 3,3-bis(hydroxymethyl)pyrrole (3H), 1,3,5-tris(hydroxymethyl)pyrrole (3I), and 2,4-bis(hydroxymethyl)pyrrole (3C) as the main fractions with a 0.28 : 0.34 : 0.15 : 0.23. The  $^{13}\text{C}$  peaks of the  $\text{CH}_2\text{OH}$

groups at 78.89(2a), 66.76(3c), 66.72(2b), 57.14(2b), 55.81(1a) and 55.65(3c) ppm were integrated and the integrals were used to calculate the mole fractions of each component.

Conducting the reaction at 25°C led to faster reactions, but similar product mixture development as at 0°C. At 4 hr, a mixture of 1-hydroxyphenylglyoxal (2a) and 1,2-bis(hydroxyphenyl)glyoxal (3c) was obtained. After 18 hours, the <sup>13</sup>C spectrum of the reaction mixture showed that the proportion of 1,2-bis(hydroxyphenyl)glyoxal (3c) started to increase. At 24 hr, 1,3,5-tris(hydroxyphenyl)glyoxal (2b) and 1,3-bis(hydroxyphenyl)glyoxal (3b) appeared. The amount of these four different hydroxyphenylglyoxals varied with time. After 8 days, 1,3-bis(hydroxyphenyl)glyoxal was the major product.

The same reaction was also carried out at 45°C and 65°C. The spectra of the samples from these two reactions were recorded. The mole fractions of each component, calculated as described previously, are listed in Tables 2.2 and 2.3. Samples obtained were similar to those of the reaction at 25°C except the time scales were even shorter as the temperature rose. Using the data in Tables 2.2 and 2.3, plots of the mole fractions of the four hydroxyphenylglyoxals against time at 45°C and 65°C are shown in Figures 2.2 and 2.3.

Pyrolic was completely consumed in less than 1 hour at 45°C. At 65°C, all pyrolic disappeared after 30 minutes, but after 90 minutes, large amounts of pyrolic were formed

Table 1.2 The Mole Fractions of Pyrolysis and the Hydrogenolysis Products in the Reaction of Pyrolysis with Formic Anhydride at 45°C

Pyrolysis Time (hr)	Pyrolysis	30	40	50	60
5	0.718	0.390	0.308	0.080	0.000
15	0.425	0.475	0.080	0.000	0.000
20	0.425	0.575	0.080	0.000	0.000
25	0.350	0.618	0.080	0.000	0.000
30	0.375	0.725	0.080	0.000	0.000
40	0.070	0.815	0.085	0.000	0.000
50	0.045	0.848	0.120	0.000	0.000
60	0.000	0.848	0.160	0.000	0.000
70	0.000	0.745	0.240	0.015	0.005
120	0.000	0.425	0.315	0.040	0.020
140	0.000	0.540	0.318	0.085	0.025
160	0.000	0.460	0.345	0.085	0.045
220	0.000	0.405	0.570	0.120	0.000
240	0.410	0.305	0.085	0.130	0.110
300	0.400	0.375	0.240	0.180	0.230
375	0.000	0.330	0.140	0.175	0.345
400	0.000	0.250	0.320	0.310	0.300
480	0.400	0.200	0.320	0.300	0.250
610	0.000	0.270	0.340	0.340	0.270
1140	0.000	0.110	0.150	0.240	0.340

Table 3.3 The Acid Functions of Pyrolic and the Hydrocarbylpyrolic Compounds in the Reaction of Pyrolic with Potassiumoxide at 85°C.

Compound Molar (mole)	Pyrolic	3A	3C	3D	3E
10	0.250	0.450	0.800	0.600	0.400
15	0.110	0.400	0.800	0.600	0.800
20	0.100	0.800	0.900	0.600	0.800
30	0.000	0.800	0.100	0.600	0.800
45	0.000	0.100	0.300	0.800	0.100
60	0.000	0.600	0.100	0.600	0.600
75	0.000	0.600	0.100	0.800	0.600
120	0.000	0.100	0.100	0.100	0.100
180	0.000	0.100	0.100	0.100	0.100
240	0.000	0.100	0.100	0.100	0.100
300	0.000	0.100	0.100	0.100	0.100
360	0.000	0.100	0.100	0.100	0.100
420	0.000	0.100	0.100	0.100	0.100
480	0.000	0.100	0.100	0.100	0.100
540	0.000	0.100	0.100	0.100	0.100
600	0.000	0.100	0.100	0.100	0.100

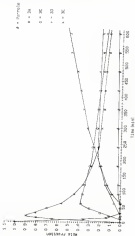


Figure 3-2 The variation with time of the rate of polymerization of styrene at  $60^\circ\text{C}$ . The curves are for different initial concentrations of styrene ( $a$ ): (a) 0.05, (b) 0.10, (c) 0.15, (d) 0.20, and (e) 0.25.

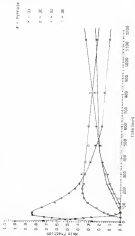


Figure 3.1 The Variation with Time of the Mole Fractions of Benzene, Hydrogen, and Nitrogen Formed at 45°C from the Reaction of Benzene (4.7 g) with Nitrogen (0.8 g) at 24, 26, 28, and 30°C.



again. This may be the result of reversible formation of 1-hydroxymethylpyrrole, the decomposition of which has been reported in the literature (STRICKER).

Compound (II) was the major product at the start of the reaction. The mole fractions of (IIa) were found to be 0.817 and 0.848 after 10 minutes at 40°C and 48 minutes at 48°C respectively. The mole fractions of intermediates (III) and (IIIb) were always less than 0.4 and 0.3 respectively. Compound (III) was the major product ultimately under all the reaction conditions.

### 3.3 Kinetics

The results in the previous section indicate that the reaction proceeds by the path shown in Scheme 2.1. The first step (I) is reversible since (IIa) decomposes into pyrrole and formaldehyde upon heating (STRICKER). The equilibrium favors (IIa) at low temperature (c. 40°C) because pyrrole is not found even in the presence of (IIa) after the reaction has proceeded for a short time. 1-hydroxymethylpyrrole reacts with one equivalent of paraformaldehyde at 40°C with a catalytic amount of NaOH to give only 1,2-bis(hydroxymethyl)pyrrole after 10 minutes. After 8 hours, a mixture of (IIa), (III), (IIIb) and (IIIc) is obtained. The half-life of (IIa) in this reaction is about 5-6 hours. This shows that (IIa) is the first intermediate



in the mechanism outlined in Scheme 3.4 and intermediate (12) is formed from (14).

Steps (14) and (15a) appear to be essentially irreversible and this is to be expected because the carbeno-carbon bonds formed are strong. However, step (15) is again an equilibrium, but one which favors the dissociation of (12) into (11) and formaldehyde because (12) is found to be the predominant product at the final stages of the reaction. Moreover, (11) is 54% decomposed into (12) and formaldehyde in about 50 hours when (11) is heated at 45°C without a solvent. The apparent difference in the positions of the equilibria in reactions 1 and 14 may reflect steric crowding in (14).

The reaction of paraformaldehyde and 2-hydroxyethylpyrrole (18) in the presence of 5400 at 1°C for 48 hr yields (11). At 45°C, the reaction of (18) with one equivalent of paraformaldehyde gives a mixture of unreacted (18), the hemiacetal of (11), and small amount of (12) after 5 minutes. The hemiacetal of (11) (which can be decomposed by heating) gives  $^{13}\text{C}$  lines at  $\delta$  128.79, 128.59, 128.25, 87.48 ( $\text{O}-\text{CH}_2-\text{OH}$ ) and 81.45 ( $\text{C}-\text{CH}_2-\text{OH}$ ) ppm. After 10 minutes 40% of (18) is converted into (12) and (11). No (12) is found even after one hour; this shows that the direct reaction of (18) with paraformaldehyde to give (11) is not an important pathway. The sole functions of (11), (12), and (13) at different times in this reaction are tabulated in Table 1.4.

Nonlinear fragments are found on all stages and are significant at the beginning of the reactions since a large

extent of ion ionization is available. The headgroups reveal themselves by showing small absorption lines close to those of their corresponding parent compounds. These lines are removed after emulsion solution has been added.

Table 3-4 The Rate Constants of (18), (19), and (20) Aqueous Time in hrs. Reaction between (18) and Formic Acids at 45°C.

Compound (Structure)	18	19	20
0	0.000	0.000	/
10	0.347	0.222	/
20	0.400	0.287	0.333
30	0.504	0.383	0.450
40	0.577	0.481	0.570

### 3.4 Discussion

The results in the previous sections show that pyrene reacts with formic acids at 1-, 2-, and 3-positions. There is no indication that electrophilic aromatic substitution occurs at the 4 position. The 1-position is the most reactive site toward formic acids but the reaction is reversible. No 2-hydroxyphenylpyrene is found in the reaction which indicates that step 11b is more favorable than step 11a:

The hemifurcal functions are important probes at the start of the reaction. As the reaction proceeds, linear and linear hemifurcals are formed since the the amount of free formaldehyde in the reaction decreases and the hydroxymethylglyoxal converts into formaldehyde also.

## 3.3 Experimentals

### 3.3.1 Spin Lattice Relaxation Time Measurements

The spin lattice relaxation time,  $T_1$ , was measured with a Varian A6-100 MHz spectrometer operating at 100MHz with  $d_6$ -DMSO as the solvent at ambient temperature. The standard software, XOL program, was used. The NMR program consisted of a two-pulse sequence for inversion recovery method. The  $90^\circ$  pulse width was 18  $\mu$ s. The equilibration time,  $t_1$ , was 40 seconds. A 63 array was automatically selected by the computer and its size depended on the length of the experiment. An interleaving process, called the cycling, was used to execute the experiments. The acquired data were analyzed by the computer.

### 3.3.2 Inverse-Gated Decoupling NMR Spectroscopy

Carbon-13 NMR spectra were recorded with a Jeol FX-100 spectrometer operating at 125 MHz with  $d_6$ -DMSO as the solvent at  $10^\circ\text{C}$ . Sample concentrations were about 1.5 g per 0.5 ml of solvent. A  $90^\circ$  pulse was used and the pulse delay was

either 8 or 24 seconds depending on whether pyruvic acid is in the sample.  $\delta_4$ -DMSO was used as a lock and its carbon peak at 38.3 ppm was used as the reference. A 20% aqueous sodium acetate solution (0.25 ml) was added to each sample to suppress hemiformal formation.

### 3.5.3 Reaction of Pyruvic and Paraformaldehyde

A mixture of pyruvic 10.1 mole, 8.7 g, paraformaldehyde 0.5 g and 10 mM (0.25 ml) solution in a 3-neck round-bottomed flask fitted with a thermometer and a magnetic stirrer was heated or cooled at the desired temperature. Samples were taken out at different time intervals and stored in a freezer before the NMR measurements were initiated.

CHAPTER 4  
HETEROCYCLE-BORITIC PHENOLIC AMINES

4.1 Introduction

Wm. A. von Ewer (1871-1949) first studied the phenol-aldehyde reaction in 1872. Its applications, synthesis and mechanism have been investigated thoroughly [THERIAULT, 1912; 1913]. It is generally agreed that under basic conditions the initial step is the formation of the five possible monomeric hydroxymethylphenols with  $\text{OH}$  groups in the *o*- and/or *p*-positions. The next step is oligomer formation which involves condensation reactions either (i) between a hydroxymethyl group of a hydroxymethylphenol and a hydroxymethyl group of another hydroxymethylphenol to give a dimethyl ether linkage, or (ii) between a hydroxymethyl group of a hydroxymethylphenol and the *o*- or *p*-OH group of phenol (or of a hydroxymethylphenol) to give a methylene bridged bisphenol derivative.

Many aldehyde-like heterocycles such as pyrazole [SPENCER], 5,5-dimethylpyrazole [THERIAULT, 1912; 1913], furan [STANLEY], imidazole [FACCHINI], and pyridine [THERIAULT] react with formaldehyde to yield hydroxymethyl derivatives. Some, such as pyrazole and furan

(TAPPI4144), can undergo further condensation reactions in acidic condition to give resins with a mechanism similar to that of phenolic resin formation. Therefore the hydroxymethyl groups of these heterocyclic modifiers may condense with phenolic nuclei or with hydroxymethyl groups of hydroxymethylphenols in the phenolic prepolymer mixture. If these hydroxymethyl derivatives of heterocycles are incorporated into the phenolic resin structure, the physical properties of the resins may be changed.

### 4.3 Styrenes

In this chapter, attempts to put styrenes and styrene rings into a phenolic resin structure are effected by reacting phenol or hydroxymethylphenols with furfural, furan, hydroxymethylfuran, furfural alcohol resin, pyrrole, or hydroxymethylpyrrole.

As a substitute for formaldehyde, furfural can improve the thermal resistance, water resistance, and adhesive property of the phenolic resins. It may be possible to put styrenes into phenolic resin structure by the following ways:

- a. condensations of the hydroxymethyl group of furfuryl alcohol with phenol nuclei
- b. condensations of the hydroxymethyl groups of the hydroxymethylphenols with furan



- c. condensations of the hydroxyethyl group(s) of furfural alcohol or 2,5-bis(hydroxyethyl)furan with the hydroxyethyl groups of the hydroxyethylphenols.

Putting furan rings into the phenolic resin structure may improve the chemical and the thermal resistance of the phenolic resins.

Pyridine polymers, e.g. poly(piphenyleneoxy)pyridine, have high thermal resistance [136861431431]. Therefore the thermal resistance of the phenolic resins may be increased by reacting pyridine compounds with phenol or hydroxyethylphenols.

#### 4-3 Phenolic Resins from Polyfuranones With Furan Polymers

##### 4-3-1 Furfural

Furfural condenses with phenol to give resins in the presence of an acid catalyst [13681431431]. It has been reported that furfural can be used to prepare modified phenolic resins with improved acid and alkali resistance [1368181818], fire resistance [13681431431], anticorrosive property [1368181818], adhesive property, water resistance and thermal stability [173681431431].

Therefore a furfural-modified phenolic resin was prepared by heating a mixture of phenol, 1% formaldehyde solution, furfural and 1% of NaOH at 150°C for 1 hour. The modified resin was tested and the test results were compared

with those of an unmodified phenolic resin, designated RD 712. The screening test results of the modified resin and resin RD 712 are listed in Table 4.1. The test procedures are described in Appendix 1.

The percent of solid of a resin should be between 70% to 90%. A resin with high percent of solid is less viscous for processing. A minimum of 75% of solid is required for the formulation of the phenolic resin binder. The percent of solid of both resins fall in the required range.

Usually the harder a resin, the better the grinding performance of the belt sander. The hardness value of a cured resin should not be below 10 DPN (Diamond Pyramid Hardness numbers). The formalin-modified resin has a lower hardness (44.6 DPN) than that of the unmodified resin (47.8 DPN). However, it is still acceptable. The hardness of a resin after water soaking should not be lower than 10 DPN. Both resin in Table 4.1 has a hardness value higher than 10 DPN. The percent of hardness retention of a resin after water soaking is a measure of the moisture sensitivity of the resin. Usually the hardness of a phenolic resin decreases after water soaking. A high percent of retention means the phenolic resin has low moisture sensitivity. The results in Table 4.1 show that the modified resin is less sensitive to moisture than the unmodified resin.

There is no clear definition for toughness. The toughness test we used is a measure of the strength of a resin toward bending. The grading ranges from 1 to 5 and 5

is the best. Both resins have the highest toughness grading.

The percent of weight loss test is a measure of the thermooxidative stability of a phenolic resin in the air at 160°C. The lower the percent of the weight loss, the higher the thermal resistance. Therefore a resin with a low percent of weight loss is desirable. The Dacron-modified resin has a lower percent of weight loss (14.4%) than resin RD 712 (14.1%).

The adhesion test is a measure of the adhesive force between the resin and the backing. The adhesion test grading ranges from 1 to 5 and 5 is the best. Both resins have the best adhesive grading.

The process of making electrode belts requires the viscosity of a resin should be in the range of 1800-4000 cps. The viscosities of the modified and the unmodified resin fall in the right range.

The gel and gel time of a resin are used to characterize them. The gel of the type of resins we prepared varies from 8 - 9.5. The gel time may be from a few minutes to one hour.

The results show that the modified resin has better thermooxidative stability and percent of hardness retention than resin RD 712 after water soaking. The thermogravimetric analysis (TGA) results in Table 4.2 support that the modified resin is more thermooxidatively stable than resin RD 712 since the former has a higher 10% weight loss temperature (the temperature at which the resin

less 18% of its weight) than that of resin RD 712. They have comparable 20% and 40% weight loss temperatures.

The results of the Pressure Bar Grinding test (the procedure is described in Appendix I) of the barfural-modified and the unmodified phenolic resin RD 712 are listed in Table 4.3. When a pressure of 150 pounds per square inches (psi) was used, the abrasive belt made from the modified resin cut a total of 387 g of carbon steel before it wore out. At the same pressure, the belt made from resin RD 712 cut only 176 g. Therefore the modified resin outperforms resin RD 712 by 14% at 150 psi. When a pressure of 300 psi was used, both belts cut more steel than at 150 psi and the belt made from the modified resin cut 18% more steel than the belt made from the unmodified resin. These grinding improvements are real since the standard deviation of this test is only a few percent.

The  $^{13}\text{C}$  spectra of the liquid barfural-modified phenolic resins show that there is always a strong carbonyl peak at 178.3 ppm due to unreacted barfural. The signal indicates that barfural does not react completely or does not react at all with phenol in the prepolymer stage. Comparing the  $^{13}\text{C}$  spectrum of the modified resin with that of resin RD 712, there is no indication that barfural actually reacted with phenol in the prepolymer formation stage. This is confirmed by heating a mixture of barfural and phenol at 150°C for 4 hours with a small amount of base. The  $^{13}\text{C}$  spectrum of the reaction mixture shows that the starting materials remain unreacted.

Table 4.3 The Screening Test Results of the Partially-modified Phenolic Resin

<u>TEST</u>	<u>MR10</u>	<u>MR12</u>	<u>Partial-modified</u>
% of Solid	34.3		73.3
Hardness(HR)	47.8		48.6
Water Absorption(HR)	21.8		30.3
% of Retention	89.9		78.8
Toughness	5		5
% of Wt. Loss	14.3		18.8
Adhesion	5		5
Viscosity(cps)	1400		1100
pH	9.25		8.80
Gel Time(min)	1203		1045

Table 4.4 The Thermogravimetric Analysis Results of the Partially-modified Phenolic Resin

<u>Resin</u>	<u>Weight Loss Temp.(°C)</u>		
	<u>10%</u>	<u>20%</u>	<u>50%</u>
MR12	298	481	550
Partial-modified	302	478	547

- Notes: 1. The rate of temperature increased is 5°C/minute;  
 the air flow is 10 cc/minute  
 2. The data are provided by the MR Company

Table 4.3 The Frequency For Standing Wave Results of the Perfluor-modified Phenolic Resins.

RESIN	150 PSI		210 PSI	
	SW	Hz	SW	Hz
NO T32	515	108	581	120
modified	567	114	655	138

Notes: The data are provided by the 3M Company.

The role of surfactant in the modified resin is unclear. Perfluor may resin is the curing step or it may simply act as a plasticizer which improves the flexibility and toughness of the resin. The differential scanning calorimetry (DSC) results in table 4.4 support the former suggestion. Each of the resins shows an endotherm in its DSC chart. The maxima of the endothermic peak ( $T_g$ ) is at  $154.1^{\circ}\text{C}$  for the unmodified resin and at  $186.7^{\circ}\text{C}$  for the modified resin. The amount of energy ( $H_g$ ) released is 176 joules per gram (J/g) by the unmodified resin and 318 J/g by the modified one. Since the two unmodified resins contain different amount of solid, the two  $H_g$  are not be compared directly unless the actual amount of solid in the resin is taken into consideration. Therefore  $H_g(10)$  values are determined by using the equation  $H_g(10) = H_g \times 100\% / \%$  of solid of the resin. The  $H_g(10)$  value for the modified resin is 728 J/g which is much higher than that (416 J/g) of the unmodified resin. This result indicates that extra bond formation or crosslinking occurs during the curing process.

Table 4.4 The Differentiated Heating Calorimetry Results of the Polystyrol-modified Phenolic resins

Resin	$\Delta H_{180}$	$T_g(^{\circ}C)$	$\Delta H_{180}$	$\Delta H_{180}/\Delta H_{180}$
RS-713	76.4	156.1	176	493
Resin 8	71.7	149.7	119	361

Note: 1.  $\Delta H_g$  = resin exotherm

$$\Delta H_{180} = \Delta H_{180}/\% \text{ of solids}$$

2. The data are provided by the RS Company.

#### 4.3.3 Hydroxyethylformate

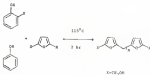
It has been reported in the literature [770820917461] that formal reacts with formaldehyde in the presence of oxalic acid at  $10^{\circ}C$  for one and a half hours to give a low-viscosity (75 cps) resin. Heating butylaryl alcohol with acid catalysts in an inert solvent also produces butylaryl alcohol resins which are thermosetting and have excellent heat and chemical resistance after curing [51812781].

The reaction of formal with paraformaldehyde in the presence of a catalytic amount of hydrochloric acid at room temperature for 18 hours gave an insoluble dark solid, which could be a formal-formaldehyde polymer (Table 4.1).



SCHEME 4.1

Heating a mixture of 4-hydroxybenzyl alcohol with either furan or tetrahydrofuran gave no reaction at all. The  $^{13}\text{C}$  spectrum showed only the peaks of the starting materials. Heating a mixture of 2,5-bis(hydroxymethyl)furan with 1 mole equivalent of either phenol or 2-hydroxybenzyl alcohol yielded only the furan polymer (Scheme 4.2) which was insoluble in DMF and other organic solvents. Phenol and 2-hydroxybenzyl alcohol remained unreacted in these reactions.



SCHEME 4.2



On the other hand, 3,4,6-trihydroxyethylphenol self-polymerized when a mixture of the phenol and 2,5-bis(hydroxyethyl)formic was heated together at 105°C for 30 minutes. The latter compound remained unreacted.

The above experiment results showed that it was difficult to introduce form rings into phenolic resin structures.

Finally a low-molecular-weight facteryl alcohol resin was prepared by heating facteryl alcohol with sulfuric acid on a steam bath for 40 minutes (Scheme 4-10). The  $^{13}\text{C}$  spectrum of the resin showed a strong peak at 17.81 ppm and also a weak peak at 18.89 ppm. There were also weak peaks at 43.14 and 62.83 ppm. This indicated that resin contained mainly methylene rather than ether linkages. A strong peak at 84.83 ppm indicated a lot of hydroxymethyl groups were present in the resin.



SCHEME 4-10

Then 25, 50 and 100% dry wt. of the resin were mixed with BB 712. These unfused resins, designated PB712-25, PB712-50 and PB712-100, were obtained. The screening test results of these three resins are listed in Table 4-1.

All the resins have lower hardness and percent of weight loss than the unmodified resin.

Table 4.5 The Densities and Results of Resins PA712-25, PA712-50 and PA712-100

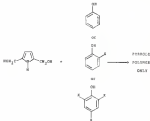
<u>TRAD<sup>TM</sup> RESIN</u>	<u>PA712-25</u>	<u>PA712-50</u>	<u>PA712-100</u>
% of Solid	88.2	76.4	73.4
Hardness (DFT)	45.8	41.9	38.4
Water Absorption	41.8	24.1	20.9
% of Retention	81.9	80.4	80.8
Toughness	8	4	3
% of Wt. Loss	13.1	19.5	21.5
Adhesive	5	5	5
Wetting Test	3	3	3

#### 4.6 Phenolic Resins Cross-Modified With Pyrazole

There is no reference in the literature to the use of pyrazole to modify the physical properties of phenolic resins. It has been reported that poly(phenylenepyrazole) is stable up to 800°C in both air and nitrogen [TAKAGAWA]. A polymer from pyrazole and pentaerythritol was heated at 800°C for 1 hour. The percent of weight loss of the polymer was found to be 20.1% which was much less than that (25%) of the standard phenolic resin, DGE 712. Therefore it was expected that the thermal resistance of the phenolic resins

might be improved by getting pyrazole rings into their structures.

When 1,4-bis(hydroxymethyl)pyrazole was heated with phenol, 2-hydroxybenzyl alcohol or 2,4,6-trihydroxymethylphenol, a black solid was formed and most likely it was a pyrazole polymer instead of a copolymer with pyrazole and phenol rings since the  $^{13}\text{C}$  NMR spectrum of the solid sample showed that the phenols remained unreacted [Scheme 4.4].



SCHEME 4.4

Pyrolic isocid also did not react with 4-hydroxyphenyl alcohol at refluxing temperature for 12 hours with or without acetic acid (Scheme 4.5).



Similar to the furan case, it was found that it was difficult to get pyrolic rings into the polymer backbone of phenolic resins. The difficulty may be attributed to the differences in reactivities between the pyrolic compounds and the corresponding phenol analogues.

A mixture of hydroxymethylpyrrole was prepared by stirring a mixture of pyrrole, paraformaldehyde and catalytic amount of NaOH at 25°C for 2 days. The  $^{13}\text{C}$  spectrum showed that the product mixture contained 2-hydroxymethylpyrrole, 4,5-bis(hydroxymethyl)pyrrole, 2,2,5-tris(hydroxymethyl)pyrrole, and 2,4-bis(hydroxymethyl)pyrrole.

Then 25, 50 and 100% (by wt) of the hydroxymethylpyrrole mixture were mixed with 80 T32. Then modified resins, PT712-25, PT712-50 and PT712-100, were obtained respectively; the screening test results of these resins are listed in Table 4-6. All the resins were harder

and more thermally stable than the standard. However they were more brittle than the P12.

Table 4.5 The Densovex Test Results of Resins P112-25, P112-50 and P112-100

TEST, RESIN	P112-25	P112-50	P112-100
% of Solid	76.8	76.1	76.3
Hardness (DIN)	55.8	43.1	51.4
Water Absorption	62.2	/	66.8
% of Retention	81.8	/	79.8
roughness	3	3	3
% of Wt. Loss	7.8	9.8	12.7
Adhesive	5	5	5
Peeling Test	1	1	1

#### 4.5 Discussion

Attempts to get furan and pyrazole rings into the structure of the phenolic resins were done but without any success. The failure could be attributed to the differences in the reactivities between phenol or hydroxyphenylphenols and the anhydride. Another reason may be the right reaction condition has not been found yet. If the latter is the cause for the failure of the copolycondensations, further investigation may lead to the right reaction condition and the successful preparations of copolymers.

The furfural-modified phenolic resin showed very promising test results. It outperformed the unmodified standard at both high pressure (100 psi) and low pressure (10 psi) grinding. Further investigation should be done in the future.

## 4.2 Experiments

### 4.2.1 Preparation of the Furfural-Modified Phenolic Resin

A mixture of phenol (475 g, 5 moles), furfural (140 g, 1.75 moles), 2% aqueous formaldehyde (500 g, 1 mole) and water (5.4 g, 1%) in a 2L round bottle fitted with a mechanical stirrer, a condenser, and a thermometer was heated at 70°C for 3 hours. The mixture was dehydrated under reduced pressure with the help of a water aspirator. The temperature of the mixture dropped rapidly to around 10°C. Then the temperature was brought up again slowly by external heating. The dehydration was stopped at about 40°C/10mm. Samples of the resin were taken out and tested according to the procedures described in Appendix 1. The resin was cooled and stored in a freezer.

### 4.2.2 Preparation of Furfural-Alcohol Resin

A mixture of furfural alcohol (100 g), water (100 g), and concentrated sulfuric acid (0.2 ml) in a 500 ml round

Isolated resin was heated on a steam bath for 48 minutes until 2 layers were formed. The exposed layer was separated and washed thoroughly with equal volumes of water 18 times, yielding 58 ml of a low molecular weight resin.  $^{13}\text{C}$  was (ppm-CDCl<sub>3</sub>) 4 155.49, 154.71, 151.48, 148.87, 148.87, 149.12, 148.28, 148.89, 148.76, 139.90, 147.54, 147.05, 138.48, 88.14, 86.40, 28.81, 27.81 ppm.

#### 4.4.3 Preparation of Phenolic-Formyl Resins

To a beaker containing the phenolic resin RB 712 (18 g) was added the formyl alcohol resin (1.5 g, 5 g, or 10 g). The resin mixture (PAC12-25, RTU12-58 or RTU12-100 respectively) was stirred thoroughly at room temperature and then cured at 70°C for 2 hours and 180°C for 18 hours. The cured resin was tested according to the testing procedures described in Appendix 3. The test results were listed in Table 4.1.

#### 4.4.4 Preparation of Phenolic-glycid Resins

A mixture of glycid (87 g, 1.8 mol), paraformaldehyde (80 g), and an acid (5.8 ml) was stirred at room temperature for 24 hours. As shown by its  $^{13}\text{C}$  spectrum, the product mixture contained 1-hydroxyethyl glycidol, 1,2-bis(hydroxyethyl)glycidol, 1,2,3-tris(hydroxyethyl) glycidol and 2,3-bis(hydroxyethyl)glycidol. Then in a beaker the phenolic resin RB 712 (18 g) was mixed thoroughly with the

hydroxyanthropipyrone mixture (2.5 g, 3.0 g, or 35 g) at room temperature to give resins PT712-25, PT712-30, or PT712-35 respectively. These resins were cured at 18°C for 3 hours and 140°C for 10 hours. The cured resins were tested according to the testing procedures described in Appendix 1. The test results were listed in Table 1.8.



## CHAPTER 5 TETRAAZANINE-CONTAINING PHTHALIC ACIDES

### 5.1 Introduction

In 1918 a dark blue substance was found during the course of the industrial production of phthalimide by passing ammonia into molten phthalic anhydride in an iron vessel in the distillate which of course contained some iron. Later this compound was shown to be iron (II) phthalocyanine [142081414]. Other metal phthalocyanines were prepared in early 1920's, mainly by A.P. Kestel [142081817, 142081817, 142081818, 142081818]

All phthalocyanine compounds transmit light in the blue-green portion of the spectrum. Ultramarine blue and iron blue were the most widely used blue pigments before the advent of phthalocyanine compounds. Now, however phthalocyanine compounds, particularly copper(II) phthalocyanine, are widely used as blue pigments and dyes because of their high tinting strength. Copper phthalocyanine has 40 times greater tinting strength than ultramarine blue and 4 times greater than iron blue [142081818]. Wide commercial applications of phthalocyanines as stable pigments and dyes has resulted in the rapid development of phthalocyanine technology in the past sixty

years. Phthalocyanine compounds exhibit remarkable stability to heat and atmospheric oxidation at 300°C or higher; these compounds are insoluble in common organic solvents, water, dilute acids and alkalis. Solubility is the biggest problem in handling phthalocyanine compounds, especially in the studio. Fortunately they are slightly soluble in high boiling aromatic solvents such as quinoline, thiophene, and skatophthalone. Phthalocyanine compounds are also soluble in cold concentrated acids; acid has been known to form solutions which yield blue precipitates on dilution.

There are three major ways to increase the solubility of the phthalocyanine compounds. The first way is to introduce polar functionalities such as sulfonic acid, tertiary amide, salt, and ammonium salt groups to one or more of the peripheral carbon atoms of the phthalocyanine molecule. The second way is to put solubilizing groups, such as alkylating groups [48,49,50,51,52], attached to the central metal in the metal phthalocyanine compounds. The third way is to incorporate alkyl chains to one or more of the peripheral carbon atoms.

All phthalocyanine compounds contain an imine electron ring (Figure 5.1).



M:  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , etc.

FIGURE 3-1

This 18 $\pi$  electron system has extremely high aromatic character, which exceeds that of benzene by a factor of 14.15. This value was determined from the magnetic susceptibilities of both compounds [HITCHCOCK]. It is proposed that the high thermal stability of a phthalocyanine compound is due to its high aromaticity. Phthalocyanine compounds also possess other interesting physical properties [KIMURA, HANAUER] such as catalytic activity, photoconductivity, semiconductivity, intense optical absorption, and chemical inertness. These properties have led to continuing research and interest in polymer phthalocyanine derivatives.

Incorporation of phthalocyanine structures in the polymeric backbone can increase the heat resistance property,

the antifluorescence, and the resistance to oxidative degradation [850001477].

Several types of phthalocyanine polymers have been reported in the literature. They are--

- a) linear phthalocyanine polymers which can have either a linear or a two-dimensional structure [850001477, 850001588, 850001687, 850001718, 850001808, 850001850, 850001918, 850001930],
- b) copolymers and copolymers loaded with phthalocyanine compounds [850001857, 850001861, 850001971],
- c) two-dimensional polymers in which the neighbouring phthalocyanine rings are linked either with or without a bridge substituent [8500009477, 850001001, 850001003, 850001004, 850001018, 850001021, 850001025, 850001187],
- d) one-dimensional polymers in which the phthalocyanine rings are connected together through the central metal ion/ligand [850001671, 850001717, 850001814, 850001918, 850001969, 850001978, 850001979, 850001981],
- e) polymers obtained from polymerization of vinyl-phthalocyanine intermediates [85000191000].

Phthalocyanine polymers have high thermal and thermooxidative properties. It has been reported that some of them are stable at 500°C and have no noticeable decomposition up to 1100°C [850001987].

There are many physical tests (applicable to for evaluating the performance of phenolic resins for coated abrasives systems). The final and decisive test is the Pressure Free Abrading Test because it simulates the real working condition for the coated abrasives. The resin are used to make coated abrasive belts which are mounted on a rotating wheel during the test. On the test carbon steel bars with which the belt is diameter are forced against a rotating belt. A tremendous amount of heat is generated due to the release of frictional energy at the point of the contact. The heat tests the ends of carbon steel bars, which are being cut by the coated abrasives, red hot. Therefore the thermal and thermooxidative stabilities of the phenolic resins used in these systems should be very important.

Although unsulfonated phenolic resins have already been considered thermal resistant, it is desirable to further improve their thermal and thermooxidative stabilities by chemical modifications. Some literature modification methods have already been mentioned in Chapter 1. However up-to-date there is only one example of improving the thermal stability of a phenolic resin by incorporating phthalocyanine ring into the polymer structure in the literature. A.S. Acher and coworkers (CHIRICIS<sup>105</sup>, CHIRICIS<sup>106</sup> and CHIRICIS<sup>107</sup>) used methyl(2,4,11,18,19-phthalocyanine)trimethanol to cure epoxy resins which included an unsulfonated novolac resin. A considerable improvement in the thermal stability of the cured materials was observed

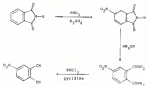
However there is still no photochemistry-mediated results reported in the literature.

Some of the attempts for improving the thermal and thermooxidative stabilities of resins with photochemistry compounds are discussed in the following sections.

### 3.2 Phenyl Resins From 4-Nitrophenylamine

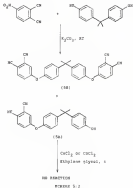
The amino group of 4-nitrophenylamine has been reported to be very reactive toward strong nucleophiles such as alcohols [85000807]. Therefore it is possible to substitute the amino group of 4-nitrophenylamine by the monomers of bisphenol A, 6,6'-biphenol, 4,4'-oxydiphenol, p-hydroquinone, etc.

Compound 4-nitrophenylamine was prepared according to the procedures outlined in Scheme 3.1. First 4-nitrophenylamine was prepared in 88% yield by the nitration of phenylamine with a mixture of nitric acid and sulfuric acid [83000455] and followed by the action of ammonium hydroxide on the nitrated product [79000008]. Dehydration of 4-nitrophenylamine with  $\text{POCl}_3$  and pyridine gave 4-nitrophenylamine in 85% yield [75000048]. The amino group gave IR peaks at 3318 and 3315  $\text{cm}^{-1}$  and the two nitro groups showed only an IR absorption at 1326  $\text{cm}^{-1}$ . The chemical shifts of the aromatic protons were at  $\delta$  8.600, 8.60, 8.611, and 8.612 ppm. The melting point was found to be 144°C (lit. m.p. 142-144°C) [75000048].



Scheme 3.4

Compound 4-methoxyphthalonitrile was converted into the phthalonitrile (15a) (47.5%) by the action of bisphthalic A with phosphorus oxychloride (POCl<sub>3</sub>) in a polar aprotic solvent at room temperature for 24 hours (Scheme 3.4). The diphthalonitrile (18a) (13.5%) was also isolated. No diphthalonitrile (18a) was found in the crude product by <sup>13</sup>C spectroscopy when a large excess of bisphthalic A was used in the reaction. A small amount of diphthalonitrile (18a) (1.8%) was the only product when the reaction temperature was increased to 80°C. The yields of the compounds (15a) and (18a) decreased to 11% and 12.5% respectively when a stronger base, NaH in DMF, was used.



The IR spectrum of (5a) showed the carbonyl absorption at 1610 and 1510  $\text{cm}^{-1}$ , and the two nitrate vibrations at 1265 and 1025  $\text{cm}^{-1}$ . There was no sign of a nitro group in the molecule. There were nitrogen lines in the  $^{13}\text{C}$  spectrum



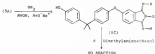
of (5A). The eighteen chemical shifts were consistent with the structure and they were at (CDCl<sub>3</sub>) δ 181.94, 174.48, 160.11, 149.41, 141.78, 139.84, 139.33, 127.89, 111.41, 101.11, 118.88, 117.89, 115.44, 109.38, 110.89, 108.49, 81.18 and 38.89 ppm. The <sup>1</sup>H spectrum of (5A) had aryl signals at δ 1.71(s, 1H) ppm, and aromatic signals at δ 6.84(d, 2H), 6.89(d, 2H), 7.15(d, 2H), 7.27(s, 2H) and 7.38(d, 2H) ppm. The melting point was found to be 150°C.

The <sup>13</sup>C NMR spectrum of (5A) was simpler than that of (5B) because of the symmetrical structure of the former. The <sup>13</sup>C lanes were at (CDCl<sub>3</sub>) δ 181.78, 181.87, 160.15, 158.19, 139.48, 138.89, 116.25, 116.19, 127.89, 115.19, 115.41, 109.79, 42.04 and 38.89 ppm. The aryl and aromatic proton signals were at (CDCl<sub>3</sub>) δ 1.72(s, 1H) and 6.7-7.1(m, 14H) ppm respectively. The two nitro groups had the same IR absorptions at 1515 cm<sup>-1</sup> by choice. The aromatic groups absorbed at 1595, 1565, 1561, and 1487 cm<sup>-1</sup>. The other vibrations occurred at 1365 cm<sup>-1</sup>. The melting point was found to be 156-157°C.

The dithianocinnoline (5C) was obtained by heating aniline gas with a methanolic solution of the phthalonitrile (5A) in the presence of sodium methoxide (Scheme 5.11). The IR spectrum showed that the phthalonitrile group was converted into the dithianocinnoline group because there were the 660cm (1313 cm<sup>-1</sup>) and 88 bending (1045 cm<sup>-1</sup>) absorptions, but no nitrile peak. The <sup>1</sup>H and <sup>13</sup>C spectra were also consistent with the structure. The <sup>1</sup>H spectrum of (5C) showed peaks at (d<sub>2</sub>-DMSO) δ 1.85(s, 6H), 2.50(s, 1H),

7.26(s,1H), 8.18(s,1H) and 8.45(s,1H) ppm. The  $^{13}\text{C}$  spectrum displayed peaks at (CDCl<sub>3</sub>) 4 141.89, 155.35, 158.88, 163.72, 167.46, 167.56, 169.29, 175.56, 178.86, 180.38, 187.37, 193.54, 195.51, 199.38, 214.88, 229.27, 41.89, and 39.73 ppm. The melting point was found to be 143 $^{\circ}\text{C}$ .

The attempts to cyclodehydrate the diimidoindoline (1C) into the corresponding phthalocyanine compound by refluxing (1C) in 2-dimethylaminopropanol failed (Scheme 5.3).



Scheme 5.3

Refluxing the compound (1A) in nitrobenzene (140 $^{\circ}\text{C}$ ) in the presence of either  $\text{CuCl}_2$  or  $\text{CuCl}$  did not give the corresponding phthalocyanine compounds (Scheme 5-4). However, the blue copper(II) phthalocyanine (1D) was obtained in 36.3% yield by refluxing the phthalonitrile (1A) in ethanol with anhydrous  $\text{CuCl}_2$  in the presence of diisobutyl[2,2,2]hexafluor (150 $^{\circ}\text{C}$ ) (Scheme 5.4).



Scheme 3.4

The copper(II) phthalocyanine (15b) dissolved in organic solvents such as acetone, DMF and DMSO to give green solutions. The copper(II) phthalocyanine (15b) had IR signals at 3130-3100, 1676, 1600 and 1518  $\text{cm}^{-1}$ . The UV absorptions were at (DMF) 279, 346, 411 and 679 nm. This UV pattern was a characteristic of the phthalocyanine compounds. The paramagnetic  $\text{Cu}^{2+}$  ion inside the phthalocyanine ring made it impossible to get a NMR spectrum for (15b). It was thought that it could be possible to get a NMR spectrum for the hydrogen analogues, phthalocyanine (15c), which was obtained similarly without  $\text{CuCl}_2$  in 20% yield (Scheme 3.4). The solubility of (15c) was too low for getting a good  $^1\text{H}$  NMR spectrum. Nevertheless a  $^1\text{H}$  NMR

spectrum was obtained and it displayed peaks at  $\delta$  8.35, 4.5-7.4, and 3-5.8 ppm. The IR absorptions of (5a) were at 3180-3500, 1600, 1500, 1400, 1300, 1200, 1170, 1010, 820 and 760  $\text{cm}^{-1}$ . The characteristic UV absorptions were at (observed) 240, 320, and 400 m $\mu$ .

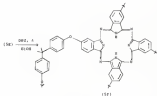
The resin GPC-DEPA-18 was prepared by heating a mixture of phenol, DOPB and 20% of the phenoloxypyrone (5a) in the presence of NaOH at 150°C for 3 hours. The screening test results of the resin are shown in Table 3-1 and are not very encouraging.

Table 3-1. The Screening Test Results of Resin GPC-DEPA-20-

<u>TEST</u>	<u>DEPA-18</u>	<u>GPC-DEPA-18</u>	<u>GPC-111</u>
% of Solid		86.4	78.0
Residual (DOP)		68.4	62.4
Water Absorption Test		59.1	49.8
% of Retention		86.4	78.0
Toughness	5	5	
% of M <sub>n</sub> Loss		17.4	14.2
Adhesive	5	5	
Wetting Test	1	1	

The diphenoloxypyrone (5a) was converted by the action of NaOH in boiling ethanol into a green solid (17a) which could be a hydrogen phenoloxypyrone polymer with the structure (5P) as shown in Scheme 3-1. The 24 and 27 ligands were considered with this structure. The IR

absorptions were at 1493, 1393, 1364, 1124, 811 and 802  $\text{cm}^{-1}$ . The characteristic IR absorptions were at (KBr) 171, 156, 813, 642, 478 and 469  $\text{cm}^{-1}$ .



#### EXPERIMENT 3.5

Another approach for the synthesis of the phthalocyanine (150) is outlined in scheme 3.6. Copper(II) 4,11,14,18-tetrakisphthalocyanine (150) was prepared by refluxing a mixture of 4-bromophthalonitrile, anhydrous  $\text{CuCl}_2$  and DMS in ethanol for 18 hours. The yield was 45%. The IR absorptions of (150) were at 1493, 1393, 1364, 1124 and 811  $\text{cm}^{-1}$ . The IR absorptions were at (KBr) 813 and 627  $\text{cm}^{-1}$ .

The phthalocyanine (151) was converted into a phthalocyanine (152) by heating the suspension with of

biophenol A with 1281 is 1282. The IR spectrum of the product of the reaction showed that only partial substitution of nitro groups occurred. The absorptions at 1524, and 1335 reveal that some nitro groups were still present in the phthalocyanine ring. The absorptions at 1675, 1608, 1586 and 1515 showed that biophenol A groups were present in the structure of the product. Therefore the structure of the product was assigned as 1281, a phthalocyanine compound with both nitro groups and biophenol A groups as its periphery.



SCHEME 5.4

### 5.3 Phthalic Acids from 4-nitrophenylnitrile

The strategy of this approach is to link a phthalic acid to a phthalocyanine compound through the reaction of the nitro group of 4-nitrophenylnitrile with an aldehyde.

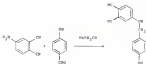
an acid or an acid derivative. A phenol compound can be converted easily to a phthalonitrile ring if it has one of these reactive functional groups. Then the newly formed phthalonitrile may be cyclotrimerized into a phthalocyanine compound with the four phenol groups around its periphery.

Newer 4-sulphaphthalonitrile was prepared by the reduction of 4-nitrophthalonitrile with either sodium dithionite (48.8%) (75AgC454) or iron metal in the presence of concentrated HCl solution in methanol (55c) (75ACR2142). The latter method gave a better yield whereas the former produced a dimeric sample (Scheme 3.7). The amino group appeared at 1498 and 1382  $\text{cm}^{-1}$  in the IR spectrum, and  $\delta$  6.71( $s$ ), 6.81 ppm in the proton spectrum. The nitrile vibrations were at 2208 and 2213  $\text{cm}^{-1}$ . The  $^{13}\text{C}$  lines were at ( $\delta_{\text{CDCl}_3}$ )  $\delta$  151.38, 125.87, 117.73, 127.66, 117.18, 126.89, 118.73, and 88.13 ppm. The melting point was found to be 149  $^{\circ}\text{C}$  (lit. mp. 181-183  $^{\circ}\text{C}$ .) (75AgC458)



SCHEME 3.7

reductive amination of *p*-hydroxyphenylaldehyde with 4-nitrophenylhydrazide in the presence of sodium cyanoborohydride gave the phenylhydrazide (5.8) in 88.38 yield (Scheme 5.8). The melting point was found to be 179°C. The number and chemical shifts of the  $^{13}\text{C}$  lines were consistent with the structure and they were at ( $\delta_{\text{p}}\text{-HMR}$ ) 4.156 84, 155.13, 154.99, 159.32, 159.81, 159.32, 117.83, 116.87, 116.39, 149.71, 115.59, 99.17 and 51.46 ppm. The pattern of the proton spectrum also agreed with the structure and the peaks were at ( $\delta_{\text{p}}\text{-HMR}$ ) 4.3-8.12, 1.81; 7.906, 7.93, 7.486, 7.87, 7.181, 6.981, 6.951, 6.91, 6.87, 6.84, 6.81 ppm. The IR spectrum contained 33 and 30 absorption bands at 3418 and 3150, and nitro vibrations at 1218 and 1248  $\text{cm}^{-1}$ .



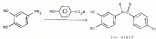
(5.8)

**SCHEME 5.8**



Refining a mixture of the phthalimide (81) and  $\text{CoCl}_2$  in ethylene glycol did not give the corresponding imide (82) phthaloyanide. The IR spectrum of the crude product showed that the nitrile groups of (81) were hydrolyzed to ester groups since strong absorption bands appeared at 1785 and 1695  $\text{cm}^{-1}$  and the nitrile absorptions disappeared. The phthalimide (81) was also not converted into the hydrogen phthaloyanide by bubbling  $\text{NH}_3$  gas into a 0.5-dimethylethanamine solution of (81) at  $110^\circ\text{C}$  (THRECHER). The phthalimide (81) remained unreacted. Refining a mixture of (81) and  $\text{SnO}$  in ethanol with or without  $\text{CoCl}_2$  failed to yield the corresponding phthaloyanide compound.

Reaction of 4-aminophthalonitrile with p-hydroxybenzoic acid in acrylonitrile in the presence of diisobutyrylcarbodiimide (83) gave only small amount of the corresponding imide. The p-hydroxybenzoic acid tended to acid-catalyze to form the ester under this condition (Scheme 3-9).



SCHEME 3-9

### 3.4 Phenolic Resins from Phthaloylbenzimidazole Derivatives

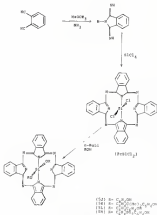
It has been reported that the two chlorides in dihalogenphthaloylbenzimidazoles ( $\text{PhOCl}_2$ ) can be displaced by phenoxide ions in fair yields ( $\text{PhOCl}_2$ ), and by the dianion anion of naphthalene to give two-dimensional conducting poly-pyrene polymers containing phthaloylbenzimidazole rings ( $\text{PhOCl}_2$ ). Therefore it is possible that the reactions of bisphenol A, p-hydroquinone, 4,4'-biphenol and 4,4'-sulfonylbiphenol can also substitute the two chlorides in  $\text{PhOCl}_2$ . The phenol moieties in the new compounds may react with formaldehyde to form hydroxymethyl groups which subsequently can cross-link with the hydroxymethyl groups to a resin.

When 1,3-dimercaptobenzimidazole was prepared by boiling ammonia gas over a methanolic solution of phthalbenzimidazole in the presence of sodium methoxide in 85% yield. Subsequent action of  $\text{HCl}$  on 1,3-dimercaptobenzimidazole gave  $\text{PhOCl}_2$  in 78% yield ( $\text{PhOCl}_2$ ). The IR spectrum of  $\text{PhOCl}_2$  was identical to that reported in the literature ( $\text{PhOCl}_2$ ). The IR absorptions were at 3400, 1600, 1470, 1400, 1330, 1260, 1145, 1030, 1000, 980, 760, 750, 704, and 400  $\text{cm}^{-1}$ . Nucleophilic substitution reactions of the mesoalkyl moieties of p-hydroquinone, bisphenol A, 4,4'-biphenol and 4,4'-sulfonylbiphenol with  $\text{PhOCl}_2$  gave the corresponding phthaloylbenzimidazole derivatives (34), (35), (36) and (37) in 45.8, 51.2, 48.8 and 14.7% yields respectively (Scheme 3-12). The yields were fair for (35) and (36), but poor for

(5c) and (5d). The reason for the difference in yield was not clear.

The  $^{13}\text{C}$ ,  $^1\text{H}$  and IR spectra of the phthalocyanine (8d) were consistent with the structure. The  $^{13}\text{C}$  spectrum showed peaks at  $\delta_{\text{C}}\text{-CDCl}_3$ : 4.145(47, 148.42, 148.75, 134.82, 131.83, 133.81 and 118.34, the  $^1\text{H}$  spectrum displayed peaks at  $\delta_{\text{H}}\text{-CDCl}_3$ : 8.46(48,49), 8.31(50, 581, 4.85(4, 499, 2.12(4,499 ppm. The phenolic proton peaks might be under the large water peak at 3.33 ppm. The IR spectrum contained a broad absorption peak at 3300-3500  $\text{cm}^{-1}$  due to the phenolic hydroxy groups. The C=O stretching bands appeared at 1781 and 1735  $\text{cm}^{-1}$ . The Si-Cl band at 468  $\text{cm}^{-1}$  disappeared and a new band appeared at 814  $\text{cm}^{-1}$  was assigned as the Si-O vibration band. The phthalocyanine ring absorptions were at 1610, 1638, 1464, 1459, 1316, 1281, 1149, 1121, 1041, 1005, 911, 754, and 711  $\text{cm}^{-1}$ .

Phthalocyanines (8d), (9a), and (9b) were characterized by IR and  $^1\text{H}$  spectra. Compound (9b) had very strong Si-O and C=O vibration bands at 1293 and 1735  $\text{cm}^{-1}$  respectively. The hydroxy group absorbed at 3300-3500, and 1147  $\text{cm}^{-1}$ . The Si-O absorption was at 811  $\text{cm}^{-1}$ . The phthalocyanine bands were at 1633, 1638, 1472, 1431, 1334, 1283, 1145, 1139, 1009, 1047, 911, 748, and 728  $\text{cm}^{-1}$ . The  $^1\text{H}$  spectrum showed peaks at  $\delta$  8.47(48,49), 8.32(4,49, 4.84(48,49, 4.52(4,49, 4.20(4,49, 3.39(4,49, 2.12(4,49 and 0.75(128,4) ppm. Phthalocyanine (9a) had two hydroxy absorptions at 3300 and 1145  $\text{cm}^{-1}$ , a Si-O band at 812  $\text{cm}^{-1}$ , two C=O



SCHEME 1.14

vibration bands at 1252 and 1212  $\text{cm}^{-1}$ , and the phenylpyrazine bands at 1628, 1522, 1431, 1216, 1201, 1149, 1112, 1081, 812, 761, and 714  $\text{cm}^{-1}$ . Its  $^1\text{H}$  spectrum was consistent with the assigned structure and contained peaks at  $\delta$  9.66(d, 2H), 9.48(s, 2H), 8.32(dd, 2H), 6.95(d, 4H), 6.21(d, 4H), 3.82(d, 4H), 1.36(d, 6H) ppm. Compound (58) had a OH absorption at 3180-3100  $\text{cm}^{-1}$ , two C-O vibration bands at 1248 and 1221, a Si-O band at 871  $\text{cm}^{-1}$ , the phenylpyrazine bands at 1612, 1512, 1412, 1312, 1202, 1187, 1221, 1098, 812, 748, and 710  $\text{cm}^{-1}$ . Its  $^1\text{H}$  spectrum displayed peaks at  $\delta$  9.62(dd, 2H), 8.34(dd, 2H), 6.93(s, 2H), 7.28(d, 4H), 6.81(d, 4H), 4.25(d, 4H), 1.44(d, 4H).

The phenylpyrazine (55) contained unchanged after it was heated with paraformaldehyde in DMF at 75°C for 3 hours in the presence of NaOH. The phenylpyrazine (58) also did not react with 95% HCHO in the presence of NaOH at room temperature for 18 hours. However after heating with a mixture of phenol and formaldehyde at 75°C, the phenylpyrazine (58) gave a soluble modified resin. These modified resins, P-618PA-5, P-618PA-10 and P-618PA-15 were prepared by using 5, 10 and 15% (by weight) of the phenylpyrazine (58) respectively. All the modified resins gave hard insoluble, unswellable, clear polymers after curing. The screening test results of these modified resins are listed in Table 3-2. All of them showed better thermooxidative stabilizer than that of 95% P-61 as they were superior to 40).

Table 5.2. The Screening Test Results of Series POLIAPA-5, POLIAPA-10, POLIAPA-20.

TEST	CRACK	POLIAPA-5	POLIAPA-10	POLIAPA-20	SR 712
% of Swell		81.0	72.0	76.0	79.0
Reduction(DRF)		84.5	68.2	52.5	58.0
% of Retention	/	/	46.0	/	78.0
Fractures	3	4	4	3	
% of Wet Loss		54.5	42.2	42.5	44.0
Adhesion	5	5	3	5	
Wetted Weight	14000	1250	/	/	
Sealing Test	/	2	/	2	
Set Time (sec)	1000	1270	/	/	
PA	0.02	0.00	/	/	

Some blue crystals were observed in the resin POLIAPA-20. They could be the unreacted phthalic anhydride (PA). This indicated that a quantity of 0.04 of PA was too much for the modification. The samples of POLIAPA-5 and POLIAPA-10 were used for Pressure Pot Curing Test. The data in table 5.2 show that they are not promising because they got more grinding residue than resin SR 712.

Table 5.3 The Increasing Test Results of P-1000-B and P-1000A-10.

RESIN	LEFT SIDE		RIGHT SIDE	
	Vol. %	% of Solids	Vol. %	% of Solids
NO. 712	1000	100	1000	100
P-1000-B	1007	81.8	1000	81.8
NO. 712	1000	100		
P-1000A-10	1042	88.4		

Note: The data was provided by the IM Company.

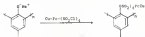
Similarly 10% of polyisoprenes (54) and (55) were used to prepare resins P-1000-10 and P-1000-20 respectively. Their thermooxidative stabilities were not superior than that of resin NO. 712 (Table 5.4), which was not expected.

Table 5.4 The Increasing Test Results of P-1000-10 and P-1000-20.

TEST	P-1000-10	P-1000-20	NO. 712
% of solid	88.4	88.8	78.8
Acidness(200F)	55.6	45.8	50.8
Toughness	5	4	3
% of Wt. Loss	14.3	13.8	14.8
Adhesive	5	5	5
Wetting Test	5	3	3

### 5.5 Phthalocyaninebisulfonfyl Chloride as Cross-Linking Agent

Copper phthalocyaninebisulfonfyl chloride (58) can be used as a cross-linking agent for resins in the presence of alkali. The cross-linking occurs through the reaction of the phenolate anions in the resin with the sulfonyl chloride groups of the phthalocyanine (58) to form sulfonates (Scheme 5-12).



SCHEME 5-11

The tetramethidium salt of copper phthalocyaninebisulfonic acid (which is commercial available) was converted into copper phthalocyaninebisulfonfyl chloride (58) quantitatively by the action of chlorosulfonic acid and followed by thionyl chloride (BACHMANN, HENRYLLAH, FINGERSTRAUS) (Scheme 5-12). Attempts to do the same conversion using POCl<sub>3</sub>, SOCl<sub>2</sub> and PCl<sub>5</sub> failed. The UV absorptions of (58) appeared at 330, 350 and 670m in DMF solution:-





Scheme 5.11

Two copper phthalocyanine-tetraalkylchloride-modified resins [PbSOCl 1 and PbSOCl 10 with different viscosities (2800 and 7000 cps respectively)] were prepared. They were prepared by heating a mixture of phenol, 17% KSO<sub>3</sub>, and resin together at 75°C for 5 hours. The solution was dehydrated partially after resin KSO<sub>3</sub> was added. Then the phthalocyanine (Cu) was added. The mixture was stirred at 70°C temperature for 5 hours and dehydrated under reduced pressure until the desired viscosity was reached. The crosslinking was supposed to be completed in the final curing stage.

The DSC curves of the copper phthalocyanine tetraalkylchloride-modified phenolic resin and the unmodified phenolic resin 20 112 were obtained on a Perkin-Elmer 800-1. There was an endotherm with a maximum at 133.7°C in the DSC curve of resin 20 112. The heat of reaction was -67.5 cal/gm (cal/g). The DSC curve of the modified resin showed two endotherms. The first was at 148.5°C with a heat of reaction of -66.27 cal/g. The second one was at 167.1°C with a much smaller heat of

reaction 1=1.55 ml/g). This second maximum indicated that there was a second slower curing mechanism for the modified resin. The curing mechanism was unclear.

The screening test results of the resin in Table 3.5 show that both modified resins were more thermally-stable than the standard, 88-712, since their  $k$  of wt. loss were much lower. The grinding test results of resins P-0001-1 and P-0001-2 (Table 3.6) show that this type of modification increases the performance of the coated abrasive system by 10%.

Table 3.5 The Screening Test Results of Polysiloxane-Isobutyl Chloride-Modified Phenolic Resins.

Test <sup>a</sup> , Resin	P-0001-1	P-0001-2	88-712
% of Solid	71.1	71.8	78.8
Acid-base(BE)	61.8	63.8	62.4
Water Swelling	61.8	65.8	68.8
% of Residue	81.8	73.2	78.8
Flouphane	8	8	8
% of Wt. Loss	11.8	9.2	18.2
Adhesion	8	8	8
Flexed type I	8888	7888	/
Wetting Test	3	1	5
600 Flex(wet)	618	1388	/
gr	8 81	8 81	/

Table 3.4. Frequency (cm<sup>-1</sup>) of Selected Vibration Bands of Resins PBOC1-1 and PBOC1-2

BAND	LEFT SIDE		RIGHT SIDE	
	CM <sup>-1</sup>	CM <sup>-1</sup>	CM <sup>-1</sup>	CM <sup>-1</sup>
NO. 111	1876	188	1871	180
PBOC1-1	1873	182	1868	178
PBOC1-2	1868	188	1876	178

Copper phenylacetylenetriethynyl chloride reacted with 4-aminophenol in DMAC to give copper phenylacetylenetriethynylamide (50) (Scheme 3-12). The sulfonamide (50) dissolved in organic solvents such as acetone and DMF to form blue solutions. The IR spectrum of (50) showed peaks at 3388-3386, 1665, 1510, 1323, 1217 and 1125 cm<sup>-1</sup>. The UV absorptions were at (DMF) 304 and 456 nm.



Scheme 3-12

It was expected that the phenol moieties of (50) could react with formaldehyde in a suitable solvent to give the hydroxyethyl derivatives which then condensed with the oligomers in the phenolic areas precipitated. However the low

solubility of (50) in aqueous solutions was not only the study of (50) by IRM, difficult, but also the application of (50) as a modifier inephotchable.

### 5.4 conclusion

One of the major problem of using phthaloynesone compounds in copolymerization with phenol-formaldehyde polymers was the low solubilities of the phthaloynesone compounds in aqueous and aqueous solutions. There was insufficient phthaloynesone compound in solution to give significant amount of copolymerization reaction. This could be the major reason for the inferior physical test results of the resins from phthaloynesones (50), (51), (52), and (53).

Copper 4,11,18,18-phthaloynesoneoctadecanoyl chloride gave resins with superior grinding performance. The reason could be the reaction between the octadecyl chloride and the hydroxy groups of the phenolic prepolymer was facile and also the phthaloynesone compound imparted good thermal resistance into the copolymers.

### 5.5 experimented

The DSC scans were run on a Perkin-Elmer DSC-2 equipped with a computer and a software called TMS. The phenolic resins were enclosed in stainless steel, high pressure vessels (Perkin-Elmer) in order to prevent volatilization

of water during the run. All runs were made using a 20°C per minute temperature ramp from 50°C to 120°C.

6-Nitrophthalimide, m.p. 150°C (lit. m.p. 150°C) [42000100] and 4-nitrophthalimide, m.p. 200°C (lit. m.p. 189-200°C) [75400100] were prepared according to the literature methods.

### 5.7.1 Preparation of 4-nitrophthalimide

Compound 6-nitrophthalimide (220 g, 1.20 mols) was suspended in pyridine (240 ml). Into this vigorously stirred suspension, phosphorus oxychloride (220 ml, 2.40 mols) was added at such a rate that the reaction maintains a temperature range of 65-70°C during the 30 minutes addition time. The same temperature was maintained an additional hour by external heating. The resulting mixture was poured onto crushed ice (2000g), and the ice slush was neutralized with 10% NaCl solution (100 ml). The purple solid was collected by filtration and dried; the residue was extracted with ethyl acetate (2x500 ml), and the purple extract was dried over anhydrous sodium sulfate, first with 2 g anhydrous saturated with NaCl (2x70 ml) and then with water (4x70 ml). Drying and reprecipitation of the extract left 46.5 g (20%) of pale yellow crystals, m.p. 161-162°C (lit. m.p. 142-143°C) [75400100].

### 5.1.1 Preparation of 4-nitrophenylisocyanide

Compound 4-nitrophenylisocyanide (8 g, 0.05 mole) was added to a mixture of methanol (100 ml) and concentrated HCl (40.5 ml) and the suspension heated to boiling. Zinc powder (10.5 g) was added in small portions over 30 minutes. The mixture was then poured into cold water and the precipitate filtered off. The crude product was recrystallized from water. Yield 5.5 g (48%). m.p. 172-173°C (lit. m.p. 171-172°C) (decoloration).

### 5.1.2 Preparation of 4-(4-(2,6-dichlorophenyl)-2,6-dimethyl-1,3,5-triazine-5-yl)-4-nitrophenyl isocyanide (13A)

A mixture of 4-nitrophenylisocyanide (1.00 g, 0.01 mole), bisphenol A (1.74 g, 0.01 mole), and potassium carbonate (1.44 g, 0.01 mole) in DMF (20 ml) was stirred at room temperature for 24 hours. The solution was neutralized with dilute HCl solution, and then extracted with  $\text{CHCl}_3$ . The extracts were combined and dried with  $\text{CaH}_2$ . The solvents were removed under reduced pressure. To the residue was added hot  $\text{CHCl}_3$  (10 ml). The suspension was cooled and the insoluble unreacted bisphenol A was filtered. The solvent was removed from the filtrate and the residue was taken up in ethanol (5 ml). The insoluble diphenylisocyanide (13A) was filtered and recrystallized from ethanol. The yield was 0.80 g (13-14%). The solvent was removed from the ethanol solution and the residue was found to be the phenylisocyanide (13A) which was recrystallized from  $\text{CHCl}_3/\text{CH}_2\text{Cl}_2$ . The yield

was 1.66 g (47.0%). For (5a), IR (neat): 3410, 2145, 2215, 2982, 1892, 1862, 1818, 1790, 1710  $\text{cm}^{-1}$ ;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  182.88, 184.88, 181.13, 180.46, 181.74, 175.34, 175.80, 177.89, 173.41, 171.36, 118.34, 147.88, 105.84, 115.68, 114.88, 108.68, 82.10, 80.38,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.71(s, 6H), 0.84(s, 3H), 0.95(s, 3H), T 124(s, 3H), T 30(s, 3H), T 34(s, 1H); m.p. 122 $^\circ\text{C}$ . For (5b), IR (neat): 3396, 2978, 1896, 1861, 1887, 1810  $\text{cm}^{-1}$ ;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  184.78, 181.87, 180.35, 175.38, 178.89, 173.88, 171.36, 170.38, 147.88, 115.38, 118.81, 106.71, 82.84, 80.45;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.71(s, 6H), 0.8-0.9(s, 3H), m.p. 180-187 $^\circ\text{C}$ .

#### 6.7.4 Preparation of acid-[2-(6-hydroxyphenyl)propyl]-thiopyran-2-thione (5c)

Ammonia gas was bubbled into a stirred mixture of 15a (12.5 g, 0.087 mol), sodium methoxide 0.81 g, and methanol (20 ml) at a moderate rate for 45 minutes. The mixture was then brought to reflux and maintained at this temperature for 3.5 hours with continued stirring and addition of ammonia. The solution was neutralized with 1N HCl and then the solvent was removed under reduced pressure. The crude product was dissolved in water (20 ml) and extracted with chloroform. The extracts were combined and dried with  $\text{MgSO}_4$ . The solvent was removed under reduced pressure. The product was recrystallized from  $\text{EtOH}/\text{MgSO}_4$ . Yield 1.7 g (73.1%); m.p. 116 $^\circ\text{C}$ ; IR (neat): 3380, 1710, 1695, 1675, 1660, 1220  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ )  $\delta$  1.84(s, 6H), 3.51(s, 3H), T 28(s, 1H), 8.18(d, 1H), 8.45(bz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$

181.65, 185.15, 188.88, 192.77, 149.48, 147.38, 146.29, 145.18, 139.88, 138.90, 137.27, 135.88, 135.31, 129.28, 114.48, 113.31, 41-45, 38.71.

5.7.3 Preparation of Compound (11) 4,12,18,25-Tetrakis(2,5-dichlorophenyl)-2,12,18,24-tetraazapentacyclo[7.7.7.1<sup>1,2</sup>.1<sup>3,4</sup>.1<sup>5,6</sup>]nona-1,3,5,7,9,11,13,15,17,19,21,23,25-dodecaene (11)

A mixture of (5a) (2.5 g, 2 mmole), anhydrous  $\text{CuCl}_2$  (8.1 g, 4 mmole),  $\text{SnO}_2$  (1.48 g, 12 mmole), and ethanol (100 ml) was refluxed for 24 hours. The dull green solid was filtered and then refluxed in ethanol (100 ml) with concentrated  $\text{HCl}$  solution (1 ml). The purple blue solid was filtered and washed with water and ethanol. Yield 0.41 g (100.0%) IR (neat) 3058-3008, 1586, 1502, 1218  $\text{cm}^{-1}$ ; UV (neat) 278, 316, 411, and 575 nm; m.p.  $>340^\circ\text{C}$ .

5.7.4 Preparation of compound 5,12,18,25-Tetrakis(2,5-dichlorophenyl)-2,12,18,24-tetraazapentacyclo[7.7.7.1<sup>1,2</sup>.1<sup>3,4</sup>.1<sup>5,6</sup>]nona-1,3,5,7,9,11,13,15,17,19,21,23,25-dodecaene (12)

The compound (12) was prepared similarly according to the procedure above for (10) except no  $\text{CuCl}_2$  was used. Yield 12% IR (neat) 3120-3048, 1616, 1606, 1581, 1508, 1483, 1218, 1212, 1212, 829, 748  $\text{cm}^{-1}$ ; UV (Ethanol) 288, 323, 484 nm,  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 2.19 (288, 281, 4.5-7 484, 288), 1.18 (323); m.p.  $>360^\circ\text{C}$ .

5.7.5 Preparation of Tetrakis(2,5-dichlorophenyl)-2,12,18,24-tetraazapentacyclo[7.7.7.1<sup>1,2</sup>.1<sup>3,4</sup>.1<sup>5,6</sup>]nona-1,3,5,7,9,11,13,15,17,19,21,23,25-dodecaene (13)

A mixture of the dihydrochloride (5a) (2.4 g, 2 mmole) and  $\text{SnO}_2$  (1.28 g, 12 mmole) in ethanol (100 ml) was refluxed for 24 hours. The silver-like green solid was



filtered, washed with ethanol, and acetone, and dried. The solid is insoluble in most organic solvents. The yield was 5.42 g (27%), IR (neat): 1681, 1592, 1344, 1118, 1013, 811  $\text{cm}^{-1}$ ; UV (DMF) 274, 318, 431, 442, 478, 498  $\text{m}\mu$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  2.88(1H, s), 3.81-3.77(m, s, p), 7.04(2H, s).

#### 3.7.8 Preparation of 4,12,20,28-Tetramicropthalimidocapric Acid (34)

A mixture of 4-micropthalimidocapric acid (1.88 g, 0.01 mole), NaOH (0.48 g, 0.02 mole), anhydrous  $\text{CaCl}_2$  (0.67 g, 0.02 mole) was refluxed in ethanol (100 ml) for 18 hours. The blue precipitate was filtered, washed with ethanol, water, and acetone. The product was dried and weighed 2.34 g (42%) IR (neat): 1682, 1578, 1344, 1148, 858  $\text{cm}^{-1}$ ; UV (DMF) 418 and 477  $\text{m}\mu$ ; n.p. 174°C.

#### 3.7.9 5-[10-(4-Hydroxyphenyl)undecyl]phthalimidocapric Acid (35)

To a methanolic solution (20 ml) of 4-micropthalimidocapric acid (2.43 g, 0.01 mole) were added 50 methanolic solution of NaOH (4 ml), p-hydroxybenzoic anhydride (1.12 g, 0.01 mole), and  $\text{CaH}_2$  (0.11 g, 0.02 mole). The solution was stirred at room temperature for 12 hours. Concentrated HCl solution was added until pH 2, and the methanol was removed under reduced pressure. The residue was taken up in 10 ml of water and extracted with ether. The aqueous solution was brought to pH 12 with NaOH solution saturated with  $\text{NaCl}$ , and extracted with  $\text{CHCl}_3$ . The  $\text{CHCl}_3$

substance was isolated, dried with  $\text{P}_2\text{O}_5$ , and reprecipitated. The crude product was recrystallized from hexane. The yield was 88.7%. m.p.  $175^\circ\text{C}$ ;  $^{13}\text{C}$  NMR ( $\text{d}_6$ -DMSO)  $\delta$  156.33, 151.43, 148.98, 139.33, 138.81, 138.33, 137.83, 128.83, 128.33, 118.72, 118.58, 98.18, 45.44;  $^1\text{H}$  NMR ( $\text{d}_6$ -DMSO)  $\delta$  9.40(s, 1H), 7.98(s, 2H), 7.48(s, 2H), 7.13(s, 1H), 6.98(s, 1H), 6.79(d, 1H), 6.38(d, 1H); IR (neat) 3418, 3134, 3042, 1536, 1498, 1423, 1373, 1218, 1018  $\text{cm}^{-1}$ ; anal.  $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_2$  Calcd: C, 72.29, H, 4.43, N, 14.43; found: C, 71.84, H, 4.37, N, 14.24.

### 5.7.10 Synthesis of 1,2-Bis(hexamethylsilyl)-1,2-dicyanobenzene

Ammonia was bubbled into stirred mixture of 1,2-dicyanobenzene (114 g, 1.5 moles), sodium methoxide 24.8 g, 8.75 moles, and methanol 114 g at a moderate rate for 48 minutes. The mixture was then brought to reflux and maintained at this temperature for 3.2 hours with continued stirring and addition of  $\text{NH}_3$ . Upon being cooled for 1 day and filtered the product yielded a crop of greenish crystals which, after being washed with ether and dried, weighed 214 g (49%). The crude product was recrystallized from methanol and ether. m.p.  $196^\circ\text{C}$  (lit. m.p.  $195\text{--}196^\circ\text{C}$ ) (4842118).

### 5.7.11 Synthesis of Bis(hexamethylphosphorodithioic)silane

In a flask equipped with a water condenser, a mechanically stirred mixture of 1,2-bis(hexamethylsilyl)-1,2-dicyanobenzene (36 g, 0.26 mole), silicon tetrachloride (61.5 ml, 0.36 mole)

and quinoline (40 ml) was brought slowly to reflux (215°C). It was maintained at this temperature for 30 minutes and then cooled to 140°C and filtered. The purple crystalline product, after being washed with quinoline, benzene, methanol, and acetone and dried at 140°C, weighed 15.8 g (78%). The product was recrystallized from 1-methylnaphthalene, m.p. 244°C; IR (neat) 1640, 1531, 1432, 1408, 1386, 1290, 1143, 1132, 1090, 1000, 916, 793, 714, and 661  $\text{cm}^{-1}$ .

#### 6.7.13 Preparation of 8,11-Dichlorophenanthro[1,2-b:4,5-b']dipyrrole (15,16a) (14)

To a solution of *p*-hydroquinone (3.3 g, 0.02 mole) in THF (40 ml) in a 250 ml 3-neck round-bottomed flask fitted with a reflux, a gas inlet, and a magnet was added *p*-ball (2.7 ml of 1.4M solution, 0.02 mole) slowly at -78°C under argon atmosphere. A white precipitate appeared after the addition. The stirring was continued for 1 hour, and then dichlorophenanthroquinodiolone (5.11 g, 0.01 mole) was added. The mixture was allowed to warm up to room temperature slowly, and refluxed for three days. The solvent was removed and the residue was suspended in water and neutralized with dilute HCl solution. The blue solid was filtered, washed with hot water, and dried. The product was then extracted in a Soxhlet extractor with acetone for three days. The yield was 15.3%.  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{-COOCD}_3$ )  $\delta$  148.47, 148.83, 149.79, 139.82, 131.43, 123.50, and 123.34;  $^1\text{H}$  NMR ( $\text{CD}_3\text{-COOCD}_3$ )  $\delta$  9.45(1H, dd), 8.53(1H, dd), 8.39(1H, dd),

2,1108,480; IR (neat) 3300-3600, 3010, 1510, 1490, 1430, 1336, 1281, 1203, 1120, 1103, 1121, 1081, 1048, 911, 860, 780, and 731  $\text{cm}^{-1}$ ; UV (ethanol) 187, 201, 220, 245, 274 m;  $n_D^{20}$  1.4470.

5.7.13 Preparation of 8,11-dihydro-2-methyl-1H-indene-1-one  
~~Chemical Abstracts 1971:1500-132~~

The procedure was the same as that for 152) except 8-methyl-4,4'-biphenyl (4.50 g, 0.02 mole) was used. Yield 61.25; IR (neat) 3100-3400, 3010, 1520, 1490, 1430, 1380, 1300, 1242, 1040, 1120, 1060, 911, 877, 740, and 723  $\text{cm}^{-1}$ ; UV (ethanol) 200, 232, 248, 262, 272 m;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ -0.01M)  $\delta$  7.110, 201, 6.9000, 401, 6.5210, 401, 6.2010, 401, 5.3010, 401, 5.2000, 400, 4.7000, 1101;  $n_D^{20}$  1.4470.

5.7.14 Preparation of 8,11-dihydro-2-methyl-1H-indene-1-one  
~~Chemical Abstracts 1971:1500-132~~

The procedure was the same as that for 152) except 4,4'-biphenyl (2.50 g, 0.02 mole) was used. Yield 49.54; IR (neat) 3100-3400, 3000, 1510, 1431, 1310, 1282, 1283, 1110, 1140, 1100, 1120, 1081, 910, 883, 702, and 734  $\text{cm}^{-1}$ ; UV (ethanol) 187, 203, 220, 242, 270 m;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ -0.01M)  $\delta$  7.0100, 401, 6.3010, 301, 6.5210, 401, 6.2010, 401, 5.3010, 401, 5.2010, 401, 4.6010, 401, 4.5010, 401, 4.2010, 401;  $n_D^{20}$  1.4470.

5.7.15 Preparation of 8,11-dihydro-2-methyl-1H-indene-1-one  
~~Chemical Abstracts 1971:1500-132~~

The procedure was the same as that for 151) except 4,4'-methylenebiphenyl (3.0 g, 0.01 mole) was used. Yield

14.15, 18 (two-fold) 1180-1000, 1403, 1325, 1272, 1201, 1180, 1271, 1185, 1265, 1221, 1168, 1400, 1067, 911, 881, 780, and 729  $\text{cm}^{-1}$ ; IR (KBr disk) 933, 813, 459, 479  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{d}_2\text{-O}_2\text{O}$ )  $\delta$  4.0(4H, s), 5.5(2H, s), 5.9(2H, s), 7.4(1H, s), 8.4(1H, s), 8.6(1H, s), 8.8(1H, s);  $n_D^{20}$  1.440 $^{\circ}\text{C}$ .

### 5.3.28 Preparation of Copper (II) 4,13,18,24-tetrakisphthaloylpyrrole-2,3,6-tricarboxylate (13)

Compound (13) was prepared by the literature method [4546(1954)] described in the following. To dry tetrahydro-4,13,18,24-tetrakis(4-phthaloylpyrrol-2,3,6-tricarboxylate) (11) (8.84 g, 0.01 mol) at  $0^{\circ}\text{C}$  in a round-bottom flask fitted with a thermometer, a condenser, a dropping funnel, and a magnetic bar was added dropwise with dichloroacetic acid (50 g, 0.11 mol). After the evolution of gas ceased, the mixture was stirred at room temperature for 1 hour and slowly heated up to  $100^{\circ}\text{C}$  in 1 hr and for a further 4 hours at  $140^{\circ}\text{C}$ . After cooling to room temperature, thiophyl chloride (6.54 g, 0.071 mol) was added over 30 minutes and the bright green mixture was stirred for a further 2 hours at  $80^{\circ}\text{C}$ . The product was isolated by pouring the cooled reaction mixture onto crushed ice with acid. The blue precipitate was washed with ice water until neutral, and finally washed with acetone. The product was dried at  $80^{\circ}\text{C}$  under reduced pressure. The yield is 7.6 g (55%); IR (KBr) 180, 408, 479;  $n_D^{20}$  1.460 $^{\circ}\text{C}$ .

### 5.2.17 Preparation of the Copper (II) 4,4',4''-tri- phenylcyclohexatrienylidene Chloride Resin

A mixture of phenol (400 g, 4 moles), 17% NaOH solution (300.5 g, 8.15 moles), and NaOH (9 g, 1%) was heated in a round bottom flask with a mechanical stirrer, a condenser, and a thermometer at 75°C for 1 hour. The solution was cooled to room temperature and NaOH (15-2 g) was added. After all the NaOH was dissolved completely in the solution, water (100 ml) was removed from the solution by vacuum distillation. Then copper (II) 4,4',4''-triphenylcyclohexatrienylidene chloride (500-100 g, 1%) was added to the resin and the mixture was stirred at room temperature for 12 hours. Water was removed from the mixture again until the desired viscosity (1000-5000 cps) was obtained. The resin was tested and stored in a freezer. IR of the cured resin (KBr pellet) 3100-2850, 2900, 2910, 2950, 1510, 1480, 1440, 1310, 1200, 1070, 1110, 1030, 800, 740, 680, 610  $\text{cm}^{-1}$ .

## CHAPTER 2 MISCELLANEOUS RESINS

### 2.1 Introduction

Epoxy resins have been modified with phenolic resins to give resins with better heat and flame resistance [40269485], higher  $T_g$  [448610818], and better adhesives [408120188]. This type of modified resins has been used to improve the thermal stability of polyamide 6 [408120288] and to make electronic equipment parts because of its good physicochemical properties [408120318].

On the other hand, phenolic resins can be modified by epoxy resins. Epoxy-modified phenolic resins have improved toughness [4026947017], and better flame-retardant [4026946646]. They are used to manufacture heat resistant films [4026943873], and friction materials [448610842]. The epoxy phenolic resins have other outstanding properties such as electrical properties, chemical resistance, heat resistance, and adhesives.

Polyisocyanates and polyurethanes copolymers have been used to modify phenolic resins too. The reactions of polyisocyanates with phenol compounds, leading to polyphenylurethanes, involve the nucleophilic attack of the phenolic hydroxy groups on the carbon atom of the

isocyanate groups followed by 1,3-bisubstitution of the R atoms (Scheme 4.1).



(Scheme 4.1)

This type of modification has been used to prepare resins with improved toughness and light resistance (BISQUINATEL), good flame resistance without the addition of flame retardants (BISQUINOLM), and also improved mechanical and dielectric properties (BISQUINOLMA).

However these modified resins are less thermally stable than the unmodified phenolic resins since the isocyanate groups tend to dissociate at high temperatures (BISQUINOLMA).



Both epoxy and urethane-modified phenolic resins have better toughness and other superior properties such as chemical resistance, flame resistance, and mechanical strength. The toughness of the resins has been considered as a major factor in the grinding performance of the phenolic resin coated abrasive systems. Therefore both types of modification have been investigated.

## 4.2 Phenolic Resins Modified With Epoxy Resins

### 4.2.1 Introduction

In this section we try to introduce a flexible polymer, such as polypropyleneimine and polyethylene glycol, into the phenolic resin structure to give a block copolymer. Unmodified phenolic resins are very brittle and they can be broken into pieces easily when they are bent or hit. It is reported that by incorporating a flexible polymer into the phenolic resin structure, the toughness can be increased. Both polypropyleneimine and polyethylene glycol are widely used in the formulations of adhesives, hence we expect that the adhesive properties can also be improved.

A flexible polymer can be bonded to a phenolic resin through an epoxy group. The epoxy ring may be introduced into either the phenolic structure or the flexible polymer structure. When a polypropyleneimine (additive) is used, the epoxy ring is put into the phenolic resin

structure by using epichlorohydrin. In the other case, polyethylene glycol is capped with epoxy groups.

#### 4.1.1 Modification with Araldite

Araldite is the trade name of a series of polyepoxypropylenamines marketed by Yacow Chemical Company. Polyepoxypropylenamines are used as epoxy curing agents and as modifiers of specialty urethane elastomer systems. As epoxy curing agents, the series of amines produced tough, clear, flexible, impact resistant coatings.

The etherification of the phenolic hydroxy group with epichlorohydrin is a good way to improve the thermooxidative stability of the phenolic resins. The cross-linking occurs through the ring-opening reactions of the glycidyl group with phenolate anions in the presence of a base catalyst.

Glycidyl phenolic resin was prepared by heating a mixture of phenol, 8% NaOH solution, and 2% water at 75°C for 2 hours. Basic sodium hydroxide and then sodium epichlorohydrin were added to the solution. The mixture was heated at 75°C for 1 hour. Unreacted epichlorohydrin and water were removed by distillation under reduced pressure. The  $^{13}\text{C}$  spectrum of the product, designated resin 8C, showed that its structure was likely to be that as shown in Scheme 4.1. There were no  $^{13}\text{C}$  lines for the free epichlorohydrin at 4.50-55, 46.18, and 13.14 ppm which indicated that epichlorohydrin reacted completely. Three new  $^{13}\text{C}$  lines appeared at 48.38, 50.48, and 47.14 ppm and

were assigned to the vinylidene group in the structure of resin EPC. The rest of the spectrum was as complicated as that of an unsulfonated phenolic resin. The peaks were in three regions. The C-20 region was in between 130 and 140 ppm, the aromatic region was in between 110 and 130 ppm. The methylene region was in the range of 45 to 55 ppm.



SCHEME 4-2

The resin EPC was cured and the test results are listed in Table 4-1. The resin was very good in toughness, even worse than that of resin EP-112. It also had a high  $T_g$  value, less, however it was a little bit harder than EP-112. The adhesion property of resin EPC was similar to that of

resin RP 712. According to its overall test results, the resin was not a potential good modifier.

Table 4-3 The Physical test results of resins RP, JEP-JEP, and RP 712.

Test \ Resin	RP	JEP-JEP	RP 712
% of Solid	41.5	41.2	39.1
hardness (DHF)	15.2	16.8	14.1
Toughness	1	2	1
% of Sol. Loss	18.8	13.2	18.8
Adhesive	0	5	0

Jethadon (JEP-2000), a linear polyacrylamide with molecular weight of ~1000, was introduced into the phenolic resin by opening the epoxy ring of resin RP by its reactive terminal primary amine groups to give a block copolymer, designated resin JEP-JEP (Table 4-3).



assignments were obtained. The spectrum showed that the epoxy ring of resin EP-9 was opened since the  $^{13}\text{C}$  lines at  $\delta$  49.18, 48.88, and 47.81 ppm disappeared. There were four new  $^{13}\text{C}$  lines at  $\delta$  69.50, 45.12, 66.48, and 67.81 which suggested that the epoxy ring was opened in two possible ways as shown in Scheme 4.3. These four  $^{13}\text{C}$  lines were assigned to the four carbons, each attached to a oxygen atom, of the two structures. The  $^{13}\text{C}$  lines of the R-C carbons of the two structures overlapped with the aliphatic peaks in between 58 and 65 ppm. The chemical shifts of the methylene protons were at  $\delta$  27.43, 28.84, and 24.96 ppm.

The test results of the resin EP-9PC are listed in Table 4.1. The results showed that resin EP-9PC was more thermally stable than and as tough as resin 80742. However it was too soft (MP = 28.4) for coated structure. To be a good adhesive for coated abrasive systems, the adhesive should has a hardness value greater than 18 MP.

### 4.3.3 Modification With Polyethylen Glycol

Polyethylene glycol had a low reactivity toward the epoxy groups of resin EP-9. There was no reaction between the hydroxy groups of polyethylene glycol and the epoxy groups of resin EP-9 after stirring them together at room temperature for 1 day. After the two starting materials were heated together, the mixture turned into a hard solid which could not be made into a casting. Therefore another approach was used. It involved capping polyethylene

glycolic with epichlorohydrin, followed by reaction with a phenolic resin.

Some polyethylene glycols with molecular weight of 400 and 1500 (PEG-400 and PEG-1500) were treated with  $\alpha$ -methyl in the order sequence to give two yellow diethylene salts respectively. The  $^{13}\text{C}$  lines of the pale yellow diethylene salts of the polyethylene glycols were at  $\delta$  45.81 and 45.77 ppm respectively.

The diethylene salts were heated with excess epichlorohydrin at  $100^\circ\text{C}$  for 16 hours (Scheme 4-4) to give carbon (PES-400-EPC) and (PES-1500-EPC). The  $^{13}\text{C}$  spectrum of the PES-400-EPC showed there were two different glycidyl groups in the product mixture and their chemical shifts were at  $\delta$  41.38, 41.48, 50.31, 50.37, 41.45, and 45.46 ppm. This suggested that a mixture of diglycidyl and monoglycidyl derivatives were formed. A small amount of unreacted epichlorohydrin was still present in the results since there were small  $^{13}\text{C}$  lines at  $\delta$  51.46, 49.54, and 45.88 ppm. A large  $^{13}\text{C}$  absorption, assigned to the polyethylene glycol  $\text{C}-\text{O}-\text{C}$  carbons, was at  $\delta$  69.88 ppm with two much smaller lines at  $\delta$  70.49 and 70.15 ppm. Similarly resin PES-1500-EPC contained a mixture of monoglycidyl and diglycidyl derivatives. The  $^{13}\text{C}$  lines of the glycidyl groups were at  $\delta$  41.58, 41.44, 41.33, 45.16, and 50.37 ppm.

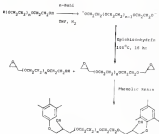


FIGURE 4-1

Resin EED-480-490 or EED-1400-490 was then stirred at room temperature for 1 day with resin no. 721 or resin ppy, a phenolic resin prepared from paraformaldehyde instead of 3,3'-formaldehyde solution. Resin ppy contained much less water than the standard since no water was used as the solvent in its preparation. Both phenolic resins were dried before the reactions to eliminate the interference of water with the epoxy rings. Since the phenolic resins were prepared under basic conditions, phenoxide ions were formed. The



nucleophilic attacks of the phenoxide ions on the epoxy rings gave the block copolymers PBO-666-EPG-gly, PBO-1380-EPG-712, and PBO-1380-EPG-gly (Scheme 4.4). Their  $^{13}\text{C}$  spectra were rather complicated, but it was found that the epoxy rings were opened since there was no  $^{13}\text{C}$  lines corresponding to an epoxy group in between 40 and 50 ppm.

The resins were cured and the results are listed in Table 4.2 together with the results of BA 712. Resins PBO-666-EPG-gly and PBO-1380-EPG-712 had higher percent of weight loss, hence less thermooxidative stable. All resins had equal or better toughness than resin BA 712. Resin PBO-666-EPG-gly had exceptional good toughness. However all resins were softer than resin BA 712. All these resins were expected since polyethylenes grafted epoxy resins were tougher, softer, and less heat resistant than phenolic resins.

Table 4.2 The Physical Test Results of Resins PBO-666-EPG-gly, PBO-1380-EPG-712, PBO-1380-EPG-gly, and BA712.

Test	<u>Resin</u> <u>PBO-666-</u> <u>EPG-gly</u>	<u>PBO-1380-</u> <u>EPG-712</u>	<u>PBO-1380-</u> <u>EPG-gly</u>	<u>BA 712</u>
% of Weight	94.1	95.1	95.2	76.2
Hardness (MPa)	48.4	47.1	47.1	54.0
Water Absorption	66.9	56.3	41.6	41.8
% of Retention	81.6	73.1	95.6	76.2
Toughness	5	3	3	3
% of Weight Loss	18.9	18.8	14.0	18.0
Adhesive	5	5	5	5

### 8.3 Chemical Reactions Between Polydiisocyanate With Polycarbonate Copolymer

The reaction between various diisocyanates with long-chain diols gave prepolymers with terminal isocyanate groups [77815448]. When a mixture of 2,4-toluenediisocyanate (TDI) and polyethylene glycol with molecular weight of 400 was heated together to give a prepolymer PEO-400-TDI (Scheme 8.8). The  $^{13}\text{C}$  spectrum of prepolymer PEO-400-TDI showed that the reaction between the isocyanate groups of TDI and the hydroxy groups of the polyethylene glycol did occur since there were two peaks at  $\delta$  69.74 and 69.38 ppm and they were assigned to the two carbons of the carbonate group next to the isocyanate groups. Other ethylene carbons of the polyethylene glycol portion gave a large peak at  $\delta$  69.77 ppm. There were four different carbonate peaks at  $\delta$  151.38, 151.55, 151.95, and 152.41 ppm. There were also four different isocyanate lines at  $\delta$  129.75, 129.81, 129.92, and 129.98 ppm. These eight chemical shifts suggested that the polyethylene glycol was end-capped by TDI in the three possible ways to give the 2,2'-, 2,4'-, 4,4'- isomers of prepolymer PEO-400-TDI.

The isocyanate groups of the prepolymer PEO-400-TDI then condensed with the hydroxy groups of either HO-TDI and pPP to give resins PEO-400-TDI-pPP and PEO-400-TDI-TDI (Scheme 8.9). The  $^{13}\text{C}$  spectrum of resin PEO-400-TDI-pPP showed that there was no unreacted isocyanate group present in the resin since the four isocyanate peaks of prepolymer



Scheme 1.1

880-880-T11 at 4 135.71, 139.81, 142.93, and 151.16 ppm disappeared. The carbamate lines overlapped with the  $^{13}\text{C}$  lines of the phenol esters, which adjacent to the phenolic hydroxy groups, lie between 150 and 160 ppm.

The resins were cured and the test results are listed in Table 8.3. Resin 880-880-880-PTF looked very promising because it had a low percent of weight loss and a high toughness value. However its grinding performance was bad, only about 48% of that of resin 88-T11. It could be due to its low hardness value and high viscosity. Resin 880-880-880-T11 gave a brittle coating with a rough surface. This could be due to the reactions between the same number of water in the resin with the isocyanate groups to give carbamic acids which decomposed into amines and carbon dioxide.

Table 8.3 The Physical Test Results of the Polyurethane-modified Phenolic Resins

Test \ Resin	880-880- 880-PTF	880-880- 880-T11	88-T11
% of Solid	82.3	86.6	81.2
Hardness (DMP)	18.8	42.9	80.3
Water Absorption	12.3	/	66.8
% of Retention	81.2	/	70.2
Toughness	5	1	5
% of WL Loss	5.8	15.4	15.4
Adhesive	5	1	5
Viscosity (cps, 25°C)	60,000	/	/

## 4.4 Conclusions

Although resin EPC was very hard, it was not tough and thermally stable. The use of Jeffamine (E-9800) to open-link the epoxy groups in resin EPC gave the resins 8EP-EPC which was too soft for making coated abrasives although the cross-linking does increase the thermal stability of the polymer. The resins 8EP-8EP-EPC-gPT, 8EP-8EP-8EP-712, and 8EP-8EP-8EP-gPT were tough, but they were soft and less thermally stable than resins 8E 712. The increasing loss results of 8EP-8EP-8EP-gPT were very promising because of the low percent of weight loss and very good toughness. However its grinding performance was only 60% of that of resin 8E 712. After cured, resin 8EP-8EP-8EP-712 gave a brittle and rough coating which was unsuitable for making coated abrasives.

## 4.5 Experimental

### 4.5.1 Preparation of 8E/8EP/8EP Phenolic Resin EPC

A mixture of phenol (84 g, 1 mole), 8E 8000 solution (142.5 g, 1.75 moles), and 8000 (12.8 g, 2%) in a 500 ml resin bottle fitted with a mechanical stirrer, a thermometer, and a condenser was heated at 75°C for 3 hours with a heating mantle. The solution was very exothermic initially so that the mantle was removed when the temperature of the reaction mixture reached 75°C. The



128.84, 127.72, 126.18, 126.06, 126.76, 126.57, 126.86, 130.47, 131.35, 134.48, 133.84, 131.47, 136.97, 137.18, 138.23, 138.94 ppm; IR of the second resin (IRs peaks): 3109-3000, 1615, 1545, 1434, 1174, 1081  $\text{cm}^{-1}$

### 6.3.3 Preparation of Glycidyl Polycarbonate Sigmoid PDC-182-127 and PDC-182-177

A solution of polycarbonate glycol (10 g) in dry THF (50 ml) was added to a 100 ml 3-neck round-bottomed flask fitted with a thermometer, a septa, and two septa with a needle on each. Triphenylmethane (0.1 g) was added to the solution as an indicator. A slow stream of nitrogen was passed into the flask through the needle. A bromine solution of  $\alpha$ -NpG (2.5 ml) was added into the solution with a syringe slowly until the solution turned red. A pale yellow resin layer appeared and was separated from the solution by decanting the solvent. Excess epichlorohydrin (20 ml) was added to the flask fitted with a condenser with a drying tube. The mixture was heated at  $100^\circ\text{C}$  for 16 hours. The excess epichlorohydrin was removed by distillation under reduced pressure:  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{-COOD}$ ):  $\delta$  78.89, 78.25, 68.85, 62.18, 61.48, 50.32, 50.12, 41.88, 41.45

### 6.3.4 Preparation of Glycidyl Polycarbonate Sigmoid-modified Phenolic Resin PDC-182-127-177, PDC-182-127-177, and PDC-182-177-177

Phenolic resin, BP 112 cc resin 177, (10 g) was put in a 100 ml round-bottomed flask. Water was removed from the resin by distillation under reduced pressure. The resin

then was dissolved in acetone (120 ml) and the solution was stirred with anhydrous  $\text{K}_2\text{CO}_3$ . The solution was filtered and the solvent was removed from the filtrate by a Rotavapor. The dry phenolic resin (10 g) was mixed with resin PBO-600-EPG or PBO-600-EPG-TEG (2 g, 10%) and the mixture was stirred at room temperature for 1 day with a mechanical stirrer to give the corresponding resin. The mixture was then cured in the usual way. IR of cured PBO-600-EPG-gly (KBr pellet): 3000-1600, 1750, 1600, 1471, 1390, 1210, 1140, 1000  $\text{cm}^{-1}$ . IR of cured PBO-600-EPG-TEG (KBr pellet): 3000-1600, 1750, 1600, 1471, 1353, 1263, 1210, 1140, 1000  $\text{cm}^{-1}$ . IR of cured PBO-600-EPG-gly (KBr pellet): 3100-1600, 2900, 1600, 1470, 1360, 1263, 1210, 1070  $\text{cm}^{-1}$ .

#### 4.3.5 Preparation of Polycarbonate Prepolymer PBO-600-TEG

A 120 ml 3-neck round-bottomed flask equipped with a magnet, a thermometer, and a dropping funnel was purged with nitrogen for 5 min. 2,4-toluenediliscyanate (10.13 g, 0.1 mole) and benzoyl chloride (8.7 g) were placed in the flask and heated to  $45^\circ\text{C}$ . Resin PBO-600 (7.5 g, 0.113 mole) was added dropwise into the solution during 1 hour. After the addition, the temperature was maintained at  $50-60^\circ\text{C}$ . The stirring was continued for 1 hour. The product was sealed in a bottle and stored in a desiccator. IR (KBr pellet): 3000-1600, 1750, 1600, 1470, 1390, 1210, 1140, 1000  $\text{cm}^{-1}$ . IR (KBr pellet): 3000-1600, 1750, 1600, 1470, 1390, 1210, 1140, 1000  $\text{cm}^{-1}$ .



119.18, 115.83, 88.71, 88.74, 88.84, 17.39; IR (neat) 1600, 1595, 1540, 1730, 3418.

4.5.6 Preparation of 2,2-bis[4-methyl-5-phenyl-5-propyl-1,3-dioxane-6,6'-diyl]propane PBO-660-TDI-PPF and PBO-660-TDI-PPF-gel

Phenolic Resin was dried in the way described before. The dry phenolic resin (20 g) was mixed with PBO-660-TDI, or PBO-1000-TDI and the mixture was stirred at room temperature for 1d hours with a mechanical stirrer. The resin was then cured and heated. For uncured resin PBO-660-TDI-PPF,  $d_4^{20}$  1.0880,  $d_4^{25}$  1.0866;  $n_D^{20}$  1.54.88, 1.54.74, 1.53.81, 1.53.85, 1.51.87, 1.50.48, 1.33.98, 1.33.40, 1.33.84, 1.33.84, 1.33.74, 1.34.53, 1.34.13, 1.27.83, 1.26.84, 1.24.47, 1.24.51, 1.24.83, 1.19.19, 1.19.87, 1.13.88, 1.13.24, 1.13.46, 1.14.45, 78.21, 83.85, 83.13, 88.13 ppm; IR of cured PBO-660-TDI-PPF (KBr pellets) 1600-1608, 1595, 1595, 1488, 1478, 1250  $cm^{-1}$ .

## REFERENCES

The system adopted for designation of references in the main body of the text is that developed by Professor A. R. Krichinsky for use in "Comprehensive Inorganic Chemistry," A.R. Krichinsky and C.W. Ross, Editors, Pergamon Press, New York (1965).

The references are designated by a number-letter code of which the first two digits (or the first four digits for references before 1960) denote the year of publication, the next one to four letters the source (journal or patent) and the final digit the page or patent number. Less common journals and books are given the code 'M' for miscellaneous. The first digit following 'M' designated the order that references occur in the text, i.e. the "2" following "M" in MM123456 means that this is the second miscellaneous reference for the year 1975 in the text that has. A list of codes (in alphabetical order) is given below followed by the journal which they represent:

<u>Code</u>	<u>Full Title</u>
ADC	Advances in Chemistry Series
ADIC	Approveds Chemis International Edition in English

AG	Angewandte Chemie
AIChE	Advances in Inorganic Chemistry and Radiochemistry
AKI	Angewandte Makromolekulare Chemie
APOL	Applied Polymer Symposia
BEF	Revue Belge
BIF	Bulletin de la Société Chimique de France
CB	Chemische Berichte or Berichte der Deutschen Chemischen Gesellschaft
CEB	Chemical and Engineering News
CL	Chemistry Letters
CEP	Chemie Patent
IC	Inorganic Chemistry
JA	Journal of the American Chemical Society
JAP	Japanese Patent
JAPT(J)	Japanese Patent (Tokyo)
JAPS	Journal of Applied Polymer Science
JCE	Journal of Chemical Education
JCS	Journal of the Chemical Society
JCS(B)	Journal of the Chemical Society, British Transactions
JCS(F)	Journal of the Chemical Society, Faraday Transactions
JEP	Journal of Chemical Physics
JEC	Journal of Industrial and Engineering Chemistry
JH	Journal of Heterogeneous Chemistry
JOC	Journal of Organic Chemistry
JOR	Journal of Organometallic Chemistry
JPH	Journal Pure Praktische Chemie

JPOC	Journal of Polymer Science Polymer Chemistry Edition
JPOL	Journal of Polymer Science Polymer Letters Edition
JPS	Journal of Polymer Science
JRP	Journal of the Russian Physical-Chemical Society
LA	Festsch. Liebigs Annalen der Chemie
RA	Revue des Sciences
RI	Simultaneous (book or journal)
RIP	Simultaneous Patent
RS	Reviews
RSP	Reichardt Patent
OSC	Organic Syntheses Collective Volume
PS	Polymer Bulletin
PSL	Proceedings of the Royal Society of London
S	Synthesis
TCS	Thermische Chemie Acta
USP	Union of Soviet Socialist Republics Patent
USP	United States Patent

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APPENDIX I  
PHYSICAL TEST PROCEDURES

1. Percent of Solid

A resin sample (1g) is weighed in an aluminum crucible. The sample is heated at 180°F (121.1°C) for 75 minutes. The weight of the solid residue is measured and the % of solid is calculated by dividing the weight of the solid residue by the weight of the sample.

2. Hardness

A liquid resin sample (0.5 g) is evenly spread on a microscope slide and cured at 70°C for 2 hours and 140°C for 20 hours. The hardness of the cured resin is measured by a Rasticon Microhardness Tester at room temperature. The hardness of the resin is expressed in terms of Diamond Pyramid Hardness number (DPH).

3. Water Soaking Test

The cured resin (from test 2) is immersed into water for 20 hours at room temperature. The resin is taken out from the water and the hardness of the cured resin is measured.

#### 8. Percent of hardness retention

Divide the hardness value from test 3 by that from test 2 and multiply by 100.

#### 9. Toughness

A sample of phenolic resin (1 g) is spread (15/1000 inch thick) on a polyester film and cured at 70°C for 2 hours and 180°C for 18 hours. The cured resin is bent around cylinders of different diameters one by one, from large to small. The cylinder around which the film cracks is recorded and the toughness is determined according to the following:

Grade	5	4	3	2	1
Diameter of cylinder	smaller 1/4"		3/8"	1/2"	3/4"

#### 10. Percent of weight loss

A resin sample (1g) is put into a preweighed aluminum crucible and cured as before. The weight of the cured sample is measured. The cured sample is then put into a furnace at 350°C for 1 hour. The residue of the sample is weighed and the % of weight loss is calculated.

### 7. Adhesive Property

A liquid resin sample (0.5 g) is spread evenly on a microscope slide and cured at 50°C for 1 hour and 100°C for 10 hours. The cured film is removed from the microscope slide with a spatula and the adhesive property is graded as follows:

<u>Grade</u>	<u>Description</u>
1	non-adhesive
2	removable with a weak force
3	removable with a mild force
4	removable with difficulty
5	cannot be removed

### 8. Wetting Test

Four drops of the resin is placed as a single spot on a filter paper inside an aluminum weighing dish. The aluminum dish with the resin is put into an oven at 100°C for 1.5 hours. The wetting property of the resin is graded as follows:

<u>Grade</u>	<u>Description</u>
1	no wetting and the resin remains as a bead
2	the filter paper is partially wetted and some of the resin remains as a bead
3	the resin wet the paper completely without bead formation



### 9. Viscosity

Viscosity of the liquid resin is measured by a rotational viscometer in centipoise.

### 10. pH

The pH of the liquid resin is measured by a pH meter.

### 11. Gel Time

A thin film of the phenolic resin (15/1000 inch thick) is coated on a microscope slide. Then the slide is put on the heating platform at 125°C of a thin film polymerizer (homemade by the IM Company). The gel time is recorded in seconds.

### 12. Grinding Test (Abrasive Pad Test)

A belt made of polyester cloth and coated with a mixture of phenolic resin and latex (B-1) is coated with 841 adhesive emulsion\* (84 g) and then a mixture of  $Al_2O_3$  and  $CrO_2$  is deposited on the belt electrostatically (450 g). The belt is heated at 80°C for 1.5 hours, and coated with a silic layer (42 g of 781 emulsion), and then heated at 80°C for 1.5 hours and 100°C for 10 hours. The belt is mounted on a test machine and rotated at high speed. Six carbon steel bars (1 inch in diameter) are pressed against the belt with pressure. The loss of the weight of the steel bars is

measured at different time intervals until it is smaller than 10 g. The total weight loss of the steel bars is calculated

Note. <sup>a</sup> A mixture of the phenolic resin, a filler, cellulose, and water with 8% of solid.

#### BIOGRAPHICAL SKETCH

REN WEI LAM was born on April 13, 1919, in Hong Kong. After he had graduated from Lung Cheung Government Technical Secondary School, Hong Kong, he started at the University of Hong Kong in September, 1938. He obtained a B.Sc. degree in 1940 and a M.Ph. degree in 1943 under the supervision of Dr. Richard F. Emmaus in the university. He transferred to the University of Florida in August, 1943 to study for a Ph.D. under the direction of Prof. Alan R. Wattley.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

  
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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



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December, 1997

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CHAS. EBERT: 4/26/00